Biopolymer nanocomposites based on Carrageenan/Graphene oxide for Environmental Application

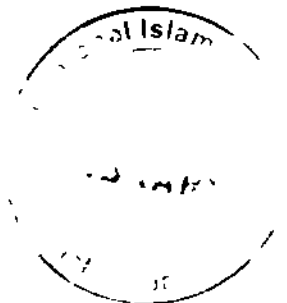**Qurat Ul Ain**
218-FBAS/MSES/F-14

Supervised By:
Dr Waqar un Nisa
Assistant Professor, Department of Environmental Sciences, IIUI

Co-Supervised By:
Dr Tariq Yasin
Deputy Chief Scientist, Department of Metallurgy and Materials Engineering.
PIEAS

INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD
Faculty of Basic and Applied Sciences
Department of Environmental Science
2016

بِسْمِ اللهِ الرَّحْمٰنِ الرَّحِيمِ

In the Name of Allāh, the Most Gracious, the Most Merciful

Biopolymer nanocomposites based on Carrageenan/Graphene oxide for Environmental Application

Qurat Ul Ain
218-FBAS/MSES/F-14

Supervised By:
Dr Waqar Un Nisa
Assistant Professor, Department of Environmental Sciences, IIUI

Co-Supervised By:
Dr Tariq Yasin
Deputy Chief Scientist, Department of Metallurgy and Materials Engineering,
PIEAS

Fall-2014

Final Year Thesis Report submitted to the Department of Environmental Sciences, as a part of the course of studies for MS Degree in Environmental Science of the International Islamic University Islamabad

INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

Faculty of Basic and Applied Sciences

Department of Environmental Sciences

Dated 22- Jan- 2017

FINAL APPROVAL

It is certified that we have evaluated the thesis report **"Biopolymer nanocomposites based on Carrageenan/Graphene oxide for Environmental Appluication"** submitted by Qurat Ul Ain(218-FBAS/MSES/F-14) and found the thesis of sufficient standard to warrant its acceptance to complete the course of studies of MS Degree in Environmental Science of the International Islamic University, Islamabad
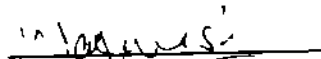
COMMITTEE

Supervisor
Name
Designation
Department
University

Dr Waqar un Nisa
Assisstant Professor
Department of Environmental Science
International Islamic University

Co-Supervisor:
Name
Designation
Department

Dr Tariq Yasin
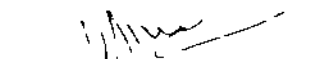Deputy Chief Scientist
DMME
PIEAS

Countersigned by:
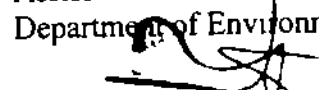**Chairperson:**
Name
Designation
Department

Dr Rukhsana Tariq
Assisstant Professor
Department of Environmental Science
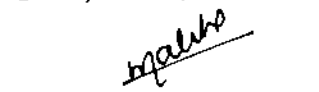
Dean. FBAS

Prof. Dr Muhammad Sher
Dean, FBAS, IIUI

Internal Examiner
External Examiner

ACKNOWLEDGEMENT

DECLARATION

I hereby declare that the work presented in this thesis is my own effort, except where otherwise acknowledged and that the thesis report is my own composition No part of this thesis has been previously presented for any other degree

Date 22-Jan-2017

Qurat ul Ain

Table of contents

List of Tables

List of Figures

List of abbreviations

CG	Carrageenan
κ-CG	Kappa- Carrageenan
GO	Graphene oxide
f-GO	Functionalized Graphene Oxide
TEOS	Tri Ethoxy Ortho Silicate
CV	Crystal Violet
FT-IR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-Ray diffraction
K_2PtCl_6	Potassium Chloroplatinate
PEPA	Pakistan Environmental Protection Agency
TDS	Total Dissolved Solids
Pb	Lead
Cd	Cadmium
Cr	Chromium
Hg	Mercury

ABSTRACT

Environmental pollution is a major concern all over the world. Among them wastewater pollution from industries has taken attention of researchers because of the serious hazards to humans and environment. Wastewater must be treated before discharge into the environment. For the treatment, natural biopolymers such as carrageenan have attracted an increasing amount of attention. The biopolymer carrageenan is natural seaweed that has been used in this study for the adsorption of crystal violet dye from the aqueous solution. Crosslinked carrageenan beads and carrageenan/graphene oxide based nanocomposites were synthesized. FTIR results showed efficient silane cross linking of carrageenan beads and strong interaction of carrageenan with silane-functionalized graphene oxide. The crosslinked carrageenan beads were further evaluated for the adsorption study of crystal violet (CV) dye. The effect of pH was studied and found that it can best behave in acidic and neutral environment. The effect of adsorbent dosage on the adsorption capacity revealed that low adsorbent dose was competent for adsorption of CV dye. The adsorption kinetics was studied by applying pseudo-first-order model and pseudo-second-order model. The experimental data best fits the pseudo second order model. By studying the effect of concentration of CV dye maximum adsorption was found at concentration of 140 mg/g. carrageenan beads were found an efficient adsorbent for the removal of crystal violet dye from the solution.

INTRODUCTION

Now a day, the world is facing an unprecedented environmental crisis where the deterioration of the Earth's environment increasingly threatens the natural resources Environmental pollution, mainly of water sources, has become public interest(Ahmad, 2009) Water from domestic sewage and industrial effluents are playing a key role in wastewater pollution Water pollution has diverse effects on human beings and living biota and is the interesting issue as it is one of the most public health concerns Wastewater pollution causes health problems like diarrhea, irritation to the skin, eyes and respiratory tract (Kazi *et al*, 2009) Wastewater from industrial effluents is also found to be carcinogenic toxic and mutagenic towards humans and animals (Jaina *et al*, 2007)

Dye industry is a major contributor in polluting the natural environment (Aksu 2005) Dyes are the pollutants present in the wastewater of leather, textile, food processing cosmetics, paper and various other dyeing industries (Bhatnagar & Jain, 2005) Structurally, they are synthetic aromatic carbon compounds bonded with various functional groups (Pearcea *et al*, 2003) Annually, $\approx$70,000 tons of 10,000 types of dyes and pigments are produced worldwide 20-30 % of these dyes are wasted during textile dyeing and finishing processes into the industrial effluents (Robinson *et al*, 2002) Textile industry consumes large amount of water and variety and large amount of chemicals like dyes throughout its manufacturing and finishing process stages

Pakistan has a leading role in textile industry It exports more than 60% of textile products to different countries Among all industries, textile industry contributes 46% to the total output produced in Pakistan In Asia, Pakistan is the 8th largest exporter of textile goods and the total contribution to the total GDP is 8 5% Toxic waste generating from different textile industries around major cities of Pakistan are progressively polluting the water bodies like rivers streams and Arabian Sea (Irfan, 2009) Most of these effluents are non-biodegradable and causes damage to the environment When these dyes are discharged into the waste streams, they are difficult to biodegrade due to complex aromatic molecular structures and synthetic origin It is also undesirable aesthetically Even a very low concentration of dyes is highly visible and unattractive (Khattri & Singh, 1998) Its treatment is also a major dilemma for environmental managers as its degradation yields carcinogenic and lethal products

Textile industry uses different dyes for coloring Among them, crystal violet is one of the important dye that is producing environmental and health problems Crystal violet (CV) is a basic dye, also known as gentian violet, methyl violet 10B and basic violet 3 (Uma *et al* . 2016) Its molecular weight is 407 98 and belongs to class tnarylmethane dyes (Mohammed *et al* 2011) Its absorption range is 589 to 598 nm on UV spectroscopy CV is used for different purposes such as pH indicator (turns violet from yellow with the transition at a pH 1 6). as active ingredient in Gram's stain and as bacteriostatic agent in medical community, in humans and animals as an external skin disinfectant and in textiles, paints and printing it is used as a purple dye (Alok Mittal *et al* . 2010) When discharged into the environment via industrial effluent it is harmful for living biota and human beings It can persist into the environment in variety of ways as it is known to be a recalcitrant molecule as it cannot be metabolized by microbes and also non-biodegradable (Chakraborty *et al* . 2011) Therefore. it is necessary to safely remove CV from industrial effluents before discharge into the environment

Contaminated water must be treated before discharge into the environment Considering the wastewater treatment techniques, well known methods are physical chemical and biological methods Physical methods include filtration, reverse osmosis. precipitation methods (sedimentation, coagulation, and flocculation). adsorption (on activated carbon, silica gel biological sludge) etc Biological process can be aerobic (revival of biological sludge in aeration basins) and anaerobic (decay and rot in stabilizing lagoons) depending on the presence or absence of oxygen Biological method also includes degradation by special fungi Chemical methods require chemicals for the discoloration of water and it includes reduction. oxidation. compleximetric methods, ion exchange and neutralization (Forgacs *et al* . 2004)

Industries such as, textile, tannery, pulp and paper industries infrequently apply these to treat their effluents because of relatively high operating costs and low removal efficiencies Among above-mentioned techniques adsorption is found to be an efficient and economic method to remove dyes and pigments It is found to be an advanced procedure for the removal of pollutants due to its low operational cost. simple design, ease of operation and insensitivity to toxic substances(Sivamani & Leena Grace. 2009)

Adsorption is the process in which the contaminant (adsorbate) in liquid form mounts up on the surface of solid adsorbent The pollutant adsorbed on the surface is called adsorbate and

the solid material on which adsorbate is accumulated is called adsorbent Adsorption is found to be an efficient method to remove pollutants from waste water as it is an efficient and economic process A good adsorbent possess qualities like easy to process, large surface area long service time, simplicity of design, high adsorption capacity, abundantly available, non-toxic to environment and biodegradable (Yan *et al* . 2014) Different low-cost adsorbents like peat. fly ash, fertilizer wastes, clay minerals, sewage sludge, and agricultural by-product such as wheat straw, barley husks etc to remove different pollutants from wastewater (Crini 2006)

Adsorption process can be affected by different factors such as pore size. specific surface area, nature, molecular size, polarity, surface functional groups and weight of adsorbent Besides this, the operating conditions, such as pH, ionic strength and temperature also affects the adsorption capacity (Site, 2001)

In first step of process of adsorption, the adsorbate molecules present in the liquid solution transfers to the surface of the adsorbent Then, these molecules move to the active sites of the adsorbent and travel along the pores of the adsorbent The adsorbate molecules adsorbs on the interior surface of the pores of the adsorbent (Rosen, 2004) The process of adsorption is shown in figure 1

Biopolymer nanocomposites can be used for the adsorption of pollutants from wastewater Biopolymer nanocomposites are the combination of polymers from biological sources and nanosized inorganic solids which forms nanostructured materials (Vanessa Leiria Campo *et al* , 2009) Biopolymer polysaccharides like carrageenan have attracted an increase interest because of its properties like they are cost effective, biodegradable, bio compatible and renewable (Crini, 2006) Biopolymer carrageenan belongs to sulphated polysaccharides family having high molecular weight obtained by the extraction of red seaweed It is composed of galactose and anhydrogalactose units coupled by glycosidic linkages (Prajapati *et al* . 2014) Graphene has taken a greater interest because of its tremendous properties like unique structure. low cost, induces no toxic effects and extraordinary electronic and mechanical properties (Yang *et al* . 2010) Because of the eco-friendly nature of the carrageenan. the present study was designed to synthesize carrageenan based nanocomposite i e Carrageenan/Graphene Oxide nanocomposite for the removal of dyes
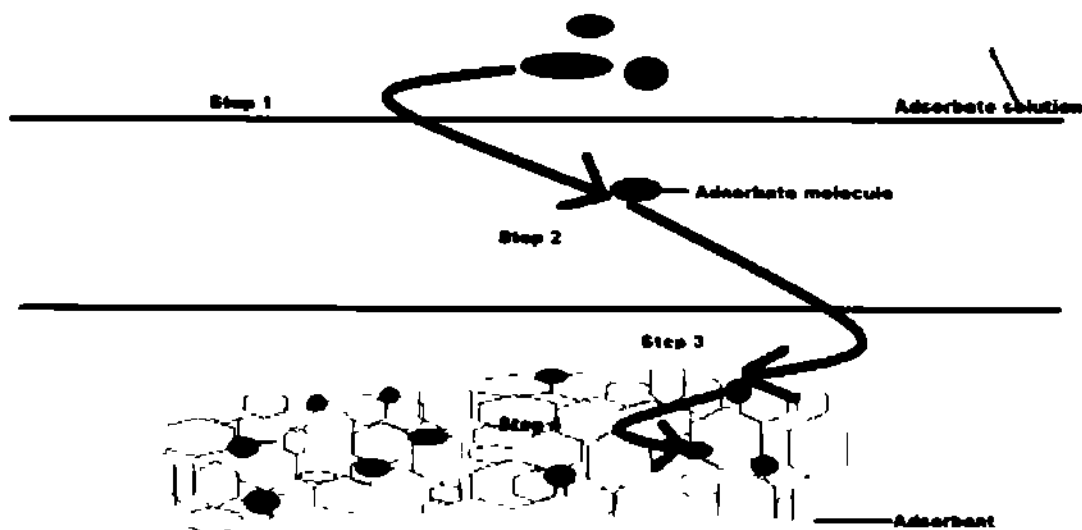
Figure 1. Schematic flow of adsorption process steps

The aim of this study is to synthesize a novel material to remediate toxic pollutants from the environment and to check the feasibility of the product on lab scale

Objectives:

1   To synthesize carrageenan based nanocomposite using graphene oxide as nanofiller **The main objective of this work is to develop the bio based nanocomposites. Attempt will be made to find the easier and cheaper way for this development and** renewable materials will be explored as the precursors.

2   To characterize of the nanocomposite by different available techniques (SEM, TGA and FT-IR)

3   **The nanocomposites will be applied for adsorption application in various fields to minimize** existing problems and challenges.

LITERATURE

REVIEW

Water pollution is a major problem around the world and chemical industry is found to be a major contributor in polluting the environment. The worldwide high level of production and extensive use of dyes generates colored wastewaters which cause environmental pollution(Saeeda et al, 2010) The environmental issues surrounding the water pollution in industrial effluent is a continuing problem for dyestuff manufacturers, dyers. finishers and water companies They consume several toxic substances for the manufacture of finished products and releases unused toxic substances as industrial waste into the environment (Aksu 2005) The discharge of industrial effluents containing toxic contaminants such as toxic metals, dyes causes negative impacts on the environment (Khattri & Singh, 2000, Ramakrishnan & Nagarajan. 2009) According to researchers, among the chemical industry organic colorant industry contributes 34% in polluting the environment (Robinson et al, 2001) Environmental scientists and regulatory bodies are continuously facing these issues and to overcome these problems. regulatory bodies enforced stringent color standards to reduce the quality of color in effluents discharge (Low & Gan, 1999) Therefore, Pakistan Environmental Protection Agency (Ministry of Climate Change) has established National Standards for Water Quality for Pakistan For example the maximum contaminant level for colour is 15 hazen Table 1 shows the maximum contaminants levels to determine water quality (Dil et al, 2008)

When wastewater containing dyes discharged into the environment via industrial effluent, it is harmful for living biota and human beings It can persist into the environment in variety of ways and also non-biodegradable Whendischarged into the freshwater bodies. some dyes are detrimental for aquatic life They decreases the growth of aquatic life since dyes reduces light penetration into water bodies thus decreases photosynthesis efficiency of aquatic plants(Ngaha et al, 2011. Slokar & Marechal, 1998, Strickland & Perkins, 1995) Some of the dyes also cause serious damage to different parts of human beings such as liver, brain. kidney. reproductive system and nervous system People working in textile industry are at high risk to bladder cancer(Bhatnagar & Jain, 2005, Chatterjee et al, 2010, Pools et al, 1978) Hence, decolorization of dye waste matter through removal of dye is an important aspect of textile wastewater treatment
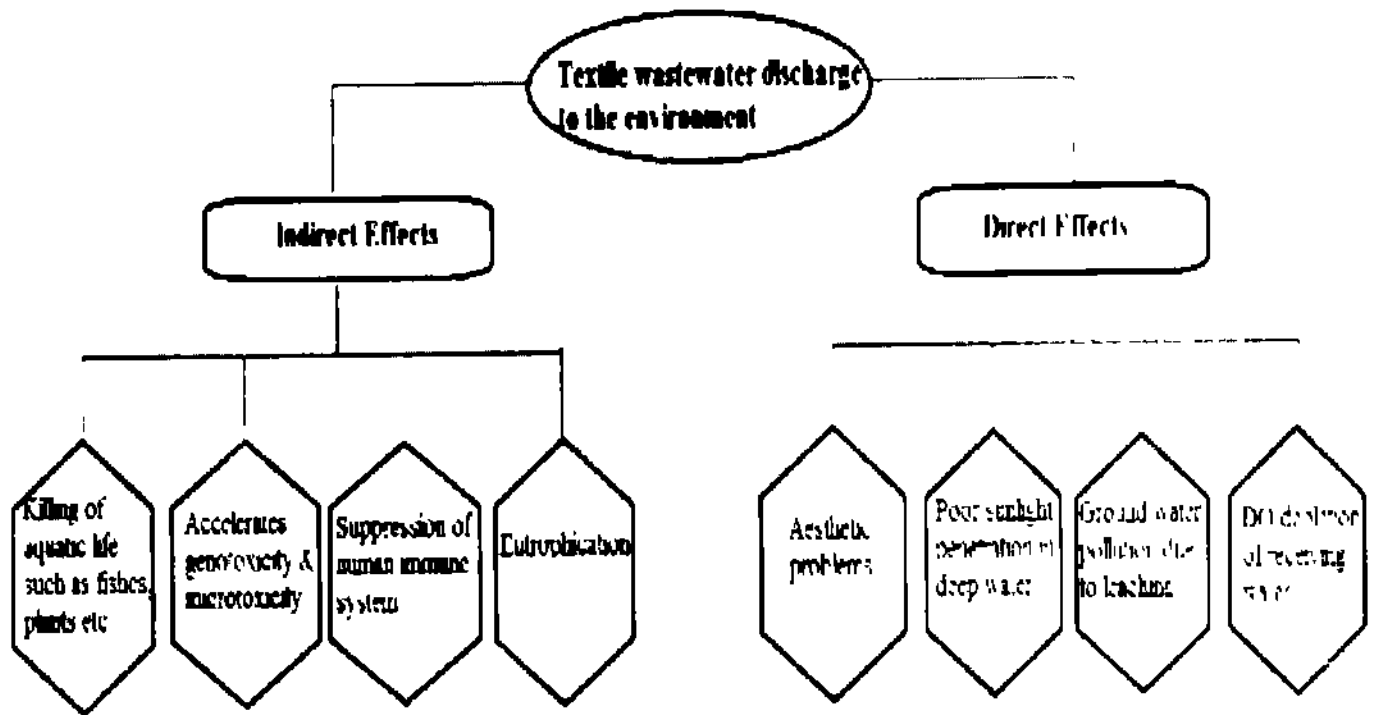
Figure: 2. Schematic diagram showing effects of textile wastewater discharge

Table: 1. Standard values of properties of water quality

Properties /Parameters	Standard Values for Pakistan	WHO Guidelines
Colour	≤15 TCU	≤15 TCU
Taste	Non objectionable/Accept able	Non objectionable/Accept able
Odour	Non objectionable/Accept able	Non objectionable/Accept able
Turbidity	‹ 5 NTU	‹ 5 NTU
Total hardness as CaCO3	< 500 mg/l	---
TDS	‹ 1000	‹ 1000
pH	6 5 – 8 5	6 5 – 8 5

The industrial effluents containing dyes are difficult to remove due to their inert properties like they are recalcitrant organic molecules, resistant to aerobic digestion, are stable to heat, sunlight and oxidizing agents Secondly, low concentration of dyes present in wastewater is difficult to remove and have high treatment costs(Ngaha et al , 2011)

Among various dyes, crystal violet (CV) is a well-known used for different industrial purposes It has been widely used as dermatological agent, veterinary medicine as biological stain, paper printing and in dye industry to give purple color to fabrics (Adak *et al* , 2005) When exposed to humans, it causes moderate eye irritation-causing aching sensitization to light or may cause permanent damage to cornea, may be absorbed through skin and cause skin and digestive tract irritation or may cause respiratory and kidney failure in extreme cases It is carcinogenic and mitotic (Mittal *et al* , 2010) It has been reported that it is also toxic to mammalian cells It was found that it is non-biodegradable and can persist in a variety of environments like in freshwater, living biota and in soil environment(Lim *et al* , 2016) Therefore, it is necessary to safely remove CV from industrial effluents before discharge into the environment

A Mittal et al (2010) reported that over the decades, industries are using different removal techniques for the removal of contaminants such as coagulation, reverse osmosis chemical precipitation, membranefiltration, solvent extraction, , photocatalyticdegradation sonochemical degradation, cation exchange membranes, electrochemical degradation biological processes and adsorption(Chatterjee et al , 2010) Industries such as, textile, tannery, pulp and paper industries infrequently apply these to treat their effluents because of relatively high operating costs and low removal efficiencies(Verma *et al* , 2012) Among above-mentioned techniques adsorption is found to be an efficient and economic method to remove dyes and pigments It is found to be an advanced procedure for the removal of pollutants due to its low operational cost, simple design, ease of operation and insensitivity to toxic substances(Seow & Lim, 2016) So far many adsorbents are used for the pollutants removal Some of the adsorbents are given in the table 2

2.1. Biopolymer nanocomposites

Biopolymer nanocomposites can be used for the adsorption of pollutants from wastewater(Crini, 2005) Biopolymer nanocomposites are the combination of polymers from biological sources and nanosized inorganic solids which forms nanostructured materials(Vanessa

Leina Campo et al , 2009) They have attracted a greater interest over the last few years Presently, they have gained greater attention because of its natural source i e from proteins and polysacchandes(Li et al , 2014) Natural polymers are non-toxic, biocompatible, cheap, locally available and biodegradable Therefore they have been used for different applications like for controlled delivery of bioactive agents, pharmaceuticals, biomedical applications and for wastewater treatment(Prajapati et al , 2014)

Biopolymers are used in the form of matrix in the nanocomposites They can be classified into non-ionic and ionic materials The ionic type consists of anionic ($-CO2$ − $-SO3$ −) and cationic pendants ($-NR^{3+}$)(Billiet et al , 2012) The presences of these ionic groups play a key role in removing pollutants from wastewater The color pollutants are either cationic or anionic molecules They show complexity with the anionic and cationic pendants of the adsorbents(Mahdavinia et al , 2012) Hence, cationic and anionic pendants can be used to remove anionic and cationic pollutants from wastewater Among the anionic polymers, carrageenan is a natural and efficient adsorbent for the removal of cationic crystal violet dye(Mahdavinia et al , 2015)

Biopolymers are of great concern in solving the biological and environmental problems In recent years, it has taken a greater interest in removing acidic and basic dyes from aqueous solutions For example, Yan et al , (2014) investigated a study for the removal of cationic dyes from water by absorbing on acrylamide/diatomic hydrogels Functional groups present on the surfaces of the biopolymers play an important to determine the capacity, effectiveness, selectivity and reusability of the adsorbent Today, adsorption is the best method which involves the interaction of functional groups present on the dyes with the functional groups present on the surfaces of adsorbent(Soedjak, 1994)

Biopolymer carrageenan belongs to sulphated polysacchandes family having high molecular weight obtained by the extraction of red seaweed(Daniel-da-Silva et al , 2008) The name Carrageenan is derived from Chondrus cripus species of seaweed Locally it is known as Carrageen Moss or Irish Moss and Carragain It is composed of galactose and anhydrogalactose units coupled by glycosidic linkages (Stucure given in figure 2)(Prajapati et al 2014) It is used in variety of food products (cheese, puddings, dairy desserts, sausages, and patties), cosmetic creams, shampoo, toothpastes and air freshener gels due to its excellent physical functional

properties, such as gelling, thickening, emulsifying and stabilizing abilities(Vanessa Feria Campo et al , 2009)

Table: 2. Different natural adsorbents for the removal of pollutants

Adsorbent	Pollutant removed by adsorption process	Reference
Kaolin	Crystal Violet Dye	(Nandi et al . 2008)
Bagasse charcoal	Acid blue dye 15	(Demirbas, 2009)
Ground shells charcoal	Acid blue red 117	(Demirbas 2009)
Redwood bark	Cd, Pb	(Randall et al 1974)
Pinus pinaster bark	Cd, Cr, Pb	(Randall et al . 1974)
Black oak bark	Cd, Pb, Hg	(Randall et al . 1974)
Activated carbon	Pb	(Vasconcelos & Beça, 1994)
Waste tea	Cd, Cr	(Orhan & Buyukgungor, 1993)
Walnut shell	Cr, Cd	(Orhan & Buyukgungor, 1993)
Chitosan	Cd, Cr, Hg, Pb	(Jha et al , 1988, Masri et al , 1974, Udaybhaskar et al , 1990)
Chitin	Pb	(Masri et al , 1974)
Orange peel (white outer skin	Cr	(Masri et al . 1974)
Orange peel (white inner skin)	Cr	(Masri et al . 1974)

In addition it has been extensively used in pharmaceutical formulations(Ghanam & Kleinebudde, 2011) Besides this, it is gaining a great interest in studying biological behavior and is identified as effective and specific compound for antitumor, anticoagulant and antiviral activities It is also proved as an efficient polysaccharide against HIV transmission after chemical modification or after coupling with antiviral agents (Buck, 2006) Studies proved that these polysaccharides can be also used as prototype for novel therapeutic agent that is expected to be more efficient and less toxic than the current chemotherapeutic agents(Li et al 2014) Depending upon the chemical structure and properties carrageenan are divided into different types are classified into λ (lambda), κ (kappa), ι (iota), U (nu), μ (mu) and O (theta)(V L Campo et al, 2009) Depending on the position and number of sulphate groups, and physico-chemical properties, e g viscosity and gelation characteristics, the most prevalent and commercially attractive types of carrageenan are kappa (1 sulphate group), iota (2 sulphate groups) and lambda (3 sulphate groups) carrageenan(Sankalia et al. 2006) The structure of kappa carrageenan is given in figure 3

2.2. Carrageenan Extraction Process

The different steps involving in the extraction of k-carrageenan are given in the figure 2 In a typical process, specie of eucheuma, hyp-nea, chondrus and turcellaria are used as a raw material Once they are received from harvesting location, they are sun bleached to dry completely and then directly sent to the processing location Before shipment they are subjected to test extraction in order to assess the quality of extract Other factors such as contents of moisture, salt and sand and non carrageenanophytes are evaluated in this stage Depending upon the texture of carrageenan, the dries seaweed is treated with 5-10% NaOH for a particular time at a temperature of 80-90 •C then, the seaweed is subjected to boiling furnace and its extract is collected in an evaporator in order to reduce the gel volume After hot extraction filtrate is again evaporated to reduce the volume of filtrate which is then extruded into cold 1-1 5% KCl solution through spinnerets The gelled threads formed are then subjected again to washing with KCl solution and are then dehydrated by pressing method The dried carrageenan is then milled to get k-carrageenan powder(Prajapati et al, 2014)

Carrageenan forms thermoreversible gels and have high viscosity which make them ideal for industrial and economic use The presence of cations controls the gelation properties of this biopolymer and its physic-chemical properties depend on the molecular weight and chemical structure(Yermak et al, 1999) Carrageenan nanocomposites have been widely used for different applications that are given in table 2

Polysaccharides like carrageenan have attracted an increase interest because of its properties like they are cost effective, biodegradable, bio compatible and renewable(Mahdavinia & Mosallanezhad, 2016) It has been used in the form of nanocomposites for a variety of applications Some of the nanocomposites are given in table 3 Because of the eco-friendly nature of the carrageenan, the present study was designed to synthesize carrageenan based nanocomposite i e Carrageenan/Graphene Oxide nanocomposite for the removal of dyes Besides its excellent properties, it has some drawbacks such as low weathering resistance, rapid dissolution in water, poor mechanical properties and low thermal property(Mehmood et al, 2007) Because of its low thermal property and the property to dissolve readily in water, carrageenan is inefficient to remove the pollutants from wastewater as high temperature would melt them and will destroy the structure Therefore, k-carrageenan needs to be chemically modified Many methods have been reported to modify the biopolymers which includes such as crosslinking, forming complexes and graft copolymers(Ngah et al, 2002)

Among them, crosslinking is found to be best method to increase its stability in harsh conditions such as low and high temperatures, to prevent its rapid dissolution in water and low pH(Sagbas et al, 2012) In order to enhance the resistance of carrageenan against temperature, pH, and to prevent dissolution in water it is necessary to be modified Some reagents such as epichlorohydrine, glutaraldehyde, Tri Ethoxy Ortho Silicate and ethyleneglycol diglycidyl ether were used to modify carrageenan(Thrimawithana et al 2010) Among them, Tri Ethoxy Ortho Silicate (TEOS) is a well known crosslinker for polysaccharides It is recognized as an efficient coupling agent to enhance thermal and mechanical properties used in composites and adhesive formulations(Bibi et al, 2015) It contains silicon, which is capable of forming chemical association between dissimilar substances(Kamal et al, 2016) The general structure of TEOS is given in figure 4 The mechanical strength can be improved by introducing a nano-filler such as Graphene, Carbon Nano Tubes (CNT's)(Bibi et al, 2015) The addition of nano-

filler not only increases the mechanical strength but also improves the rate and dye adsorption capacity

Seaweed

(Eucheuma,Hyp-Nea, Chondrus, Furcellaria)

Sun Bleaching

Alkali Treatment

Washing with KCl

Hot Extraction

Filtration

Gelling

Cutting   Kcl Precipitation

Gel Process   Evaporation

Hydraulic Press   Kcl Precipitation

                                          (In 1-1 5% KCl Soln)

Drying Chamber   Washing

Milling   Press or Freeze Thaw

Carrageenan Powder   Chopping

                          Milling

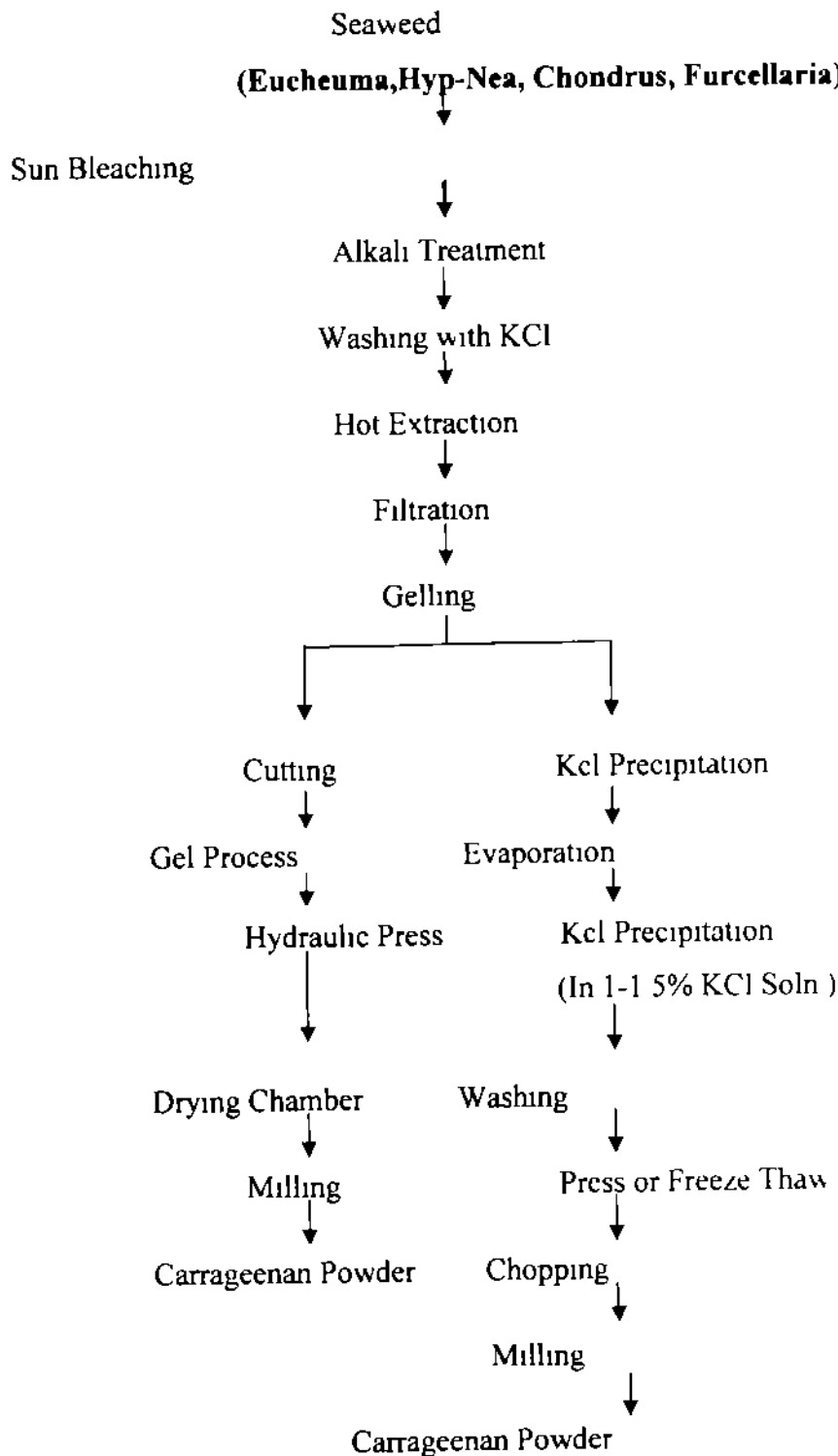   Carrageenan Powder

Figure: 3. Flow chart of carrageenan manufacturing

Recently, Graphene has been used as an excellent nano-filler in various nanocomposites For example Yan et al (2014)reported the introduction of graphene in the chitosan biopolymer to increase the mechanical strength and rate of adsorption of Copper in the study of Adsorption behavior of cross-linked chitosan modified by graphene oxide for Cu (II) removal

Graphite contains a natural basic building block known as graphene Graphene has taken a greater interest because of its tremendous properties like unique structure. low cost. induces no toxic effects and extraordinary electronic and mechanical properties(Loryuenyong et al, 2013) But it has a drawback that it forms agglomerates, which leads to insolubility which inevitably affects the dispersion of graphene before introduction in graphene based nanocomposites(Krolow et al, 2011) To overcome this problem Graphene Oxide (GO) can be used as a novel adsorbent which can be synthesized from low cost graphite It possesses high water solubility and large specific surface area because there are large numbers of oxygenous groups like hydroxyl, carboxyl, epoxy on the graphitic backbone of GO(Zhao et al, 2011) The structure of graphene and graphene oxide is given in figure 5 The compatibility of carrageenan with GO is found to be unsatisfactory because of the non-homogeneous dispersion of graphene in the matrix and the weak interfacial interactions between the graphene and the matrix To overcome this problem, functionalized GO (f-GO) can be used as nano-filler in the biopolymer matrix(Li et al, 2015)

During past several years, the dispersion and interface of GO with the biopolymer matrix has been improved by using various surface and functionalization techniques Among these treatments, silane coupling agents have gained more interest because it increases the dispersability as well as strengthens the interfacial bonding between graphene and matrix(Wan et al, 2014) Generally, the functional groups such as ethylene, amine, epoxy, thiohydroxy present on the GO surface covalently bonds with the polymer matrix(Li et al, 2015). thus leading to enhanced properties of carrageenan and GO

Considering the excellent adsorption ability of GO and good stability in water and due to the presence of sulphate groups present in carrageenan it is expected that the crosslinked carrageenan/f-Go will be a super adsorbent In initial step, the cross-linked carrageenan beadswere prepared and the preparation conditions were optimized In the preliminary report, we have investigated the preparation of crosslinked carrageenan. characterization of carrageenan beads
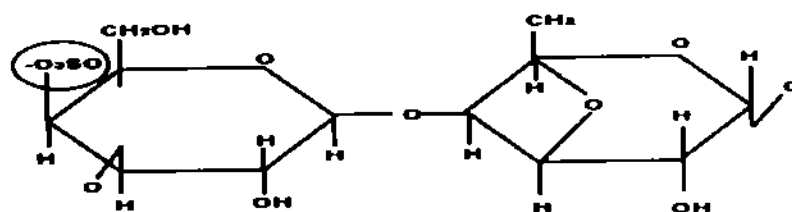
Figure: 4. Structure of Carrageenan
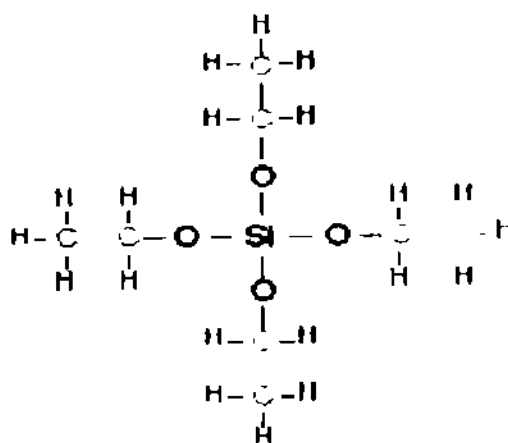
Figure: 5. Structure of TEOS

Graphene   Graphene oxide
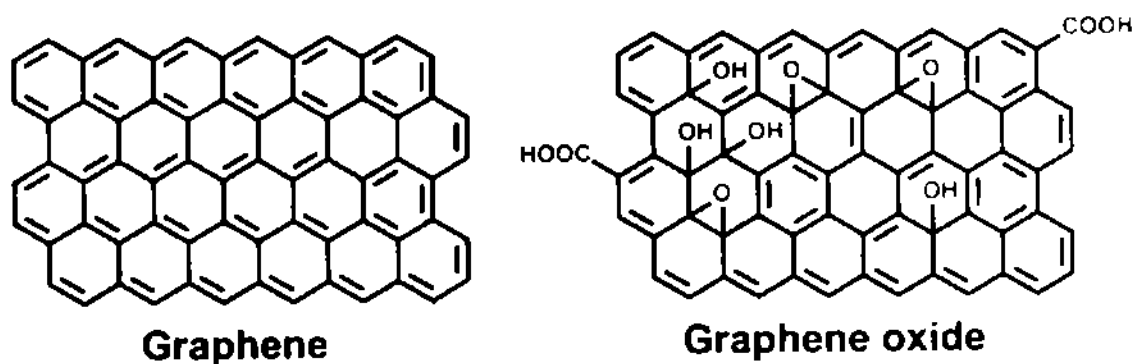
Figure: 6. Structure of Graphene and Graphene Oxide

Table:3. Comparative studies showing carrageenan composites for different applications

Nanocomposite	Initiator/Cross-linker used	Characterization	Application	Reference
CA/RGO	AgNO₃	UV-vis spectroscopy, FTIR, SEM, and XRD	Adsorption of Methylene Blue	Zheng et al, 2015
Magnetic kappa-carrageenan/PVA	K⁺ Solution	TEM, SEM, XRD, TGA, VSM	Adsorption of Crystal Violet	Mahdavinia et al 2014
Microparticles of ıCAR and kCAR	Glutaraldehyde	SEM, XRD FT-IR	Removal of Metoprolol from aqueous samples	Nanaki et al, 2015
CarAlg/MMt	Acrylamide (AAm), methylenebisacrylamide (MBA), and ammonium persulfate (APS)	TEM, SEM XRD	Adsorption of crystal violet	Mahdavinia et al, 2013
j-Carrageenan coated magnetic iron oxide	-------	FTIR, TGA, SEM, XRD, VSM	Removal of methylene blue	Salgueiro et al, 2013
Kappa-carrageenan-g-poly(acrylamide)/ sepiolite	Methylenebisacrylamide and ammonium persulfate	FTIR, SEM, TEM, TGA	Adsorption of crystal violet	Mahdavinia and Asgari 2013
Carrageenan/poly (vinyl alcohol)/montmorillonite	K⁺ ions	FTIR, SEM, XRD, TEM	Removal of crystal violet dye	Hosseinzadeh et al 2015

Nanocomposite	Initiator/Cross-linker used	Characterization	Application	Reference
Carra/ Na-MMt	Acrylamide and Methylenebisacrylamide	SEM, XRD	Adsorption of Methylene Blue	Mahdavinia, et al 2014
κ-carrageenan-g-poly(methacrylic acid)	Methylenebisacrylamide	FT-IR, XRD, SEM, TEM and VSM	Crystal Violet adsorption	Gholami et al , 2016
Carrageenan/ sodium montmorillonite	Methylenebisacrylamide	XRD, FTIR, SEM, TEM	Adsorption of crystal violet	Mahdavinia et al , 2012
Carrageenan grafted copolymer with poly (vinyl alcohol)	Potassium persulphate	ATR-FTIR, tensile strength, elongation at break, swelling ratio, contact angle	Grafting	Sukhlaaieda and Riyajan 2013
κ-carrageenan/sodium alginate hydrogel nanocomposite	K^+/Ca^{2+} ions	TEM, SEM, EDS, XRD, FTIR, and VSM	Drug Delivery	Mahdavinia et al 2014
Magnetic κ-carrageenan	Chitosan	FTIR,SEM,TEM, VSM,TGA	Adsorption of Methylene blue from aqueous solution	Mahadivinia and Mosallanezhad 2016
Semi-IPN carrageenan-based nanocomposite	Methylenebisacrylamide	SEM, XRD	---------------	Mahdavinia et al , 2009
Carrageenan/ laponite RD	laponite	XRD, SEM, TEM	Removal of crystal violet dye	Mahdavinia et al , 2012
Magnetic and K+-cross-linked kappa-carrageenan nanocomposite beads	Fe_3O_4 nanoparticles	SEM, VSM, TGA, TEM	Adsorption of crystal violet	Mahdavinia etal , 2014

and study of parameters such as contact time. initial concentration of crystal violet and adsorbent dosage for the adsorption of crystal violet According to literature review. crosslinked carrageenan beads have not been reported so far In the second phase. carrageenan/f-Go composite is prepared to check the maximum adsorption of crystal violet The structural properties of composite are characterized by infrared spectroscopy The synthesized carrageenan based nanocomposite is expected to be an efficient adsorbent for the removal of crystal violet dye from aqueous solutions

MATERIAL AND METHODS

The present methodology is designed to synthesize an efficient, cheap and biodegradable adsorbent for the removal of cationic dye i e crystal violet This chapter will describe the detailed synthesis of carrageenan based nanocomposite, its characterization techniques used to analyze its properties and adsorption models applied to describe the trends of adsorption process

3.1. Reagents and Materials

For the preparation of carrageenan beads and carrageenan-based nanocomposites carrageenan was purchased from Sigma Aldrich, Crystal Violet from Micko Industrial Chemical Co and synthetic graphite from Sigma Aldrich All other chemicals used were analytical grade reagents without further purification

3.2. Synthesis

3.2.1. Synthesis of cross-linked carrageenan beads

1 g of carrageenan powder was dissolved in 30 ml of water at 80° C temperature for 1 hour Final volume after complete dissolution was 20 ml 4 ml carrageenan solution was taken in a syringe and was dropped in 5 ml ethanol for hardening of beads (Q_2 beads) The hydrolyzed TEOS (1200 μl) was added slowly in Q_2 beads The beads were poured into dishes and then dried for 2 days. The beads were further treated to check the stability

3.2.2. Synthesis of Graphene oxide

Graphene oxide was prepared by improved Hummer's Method (Paulchamy et al . 2015) In a typical procedure, first of all graphite was purified by taking 8 ml of HCl and 25 ml of water into a flask containing graphite (1g) The mixture was stirred at room temperature for 25-30 minutes and then decanted with distilled water until pH reaches to 7 and color changes to silverish black. In the second step, the expanded graphite was oxidized to graphite oxide followed by mixing expanded graphite into 40 ml of H_2SO_4 and 3 9 ml of H_3PO_4 (9 1) The mixture was stirred for 30 minutes on ice bath at 0 °C After 30 minutes, when the temperature was raised to 5 °C $KMnO_4$ (1 8 g) was added and stirred for 30 minutes Distilled water (10-15 ml) was added into the mixture and stirred for 15-20 minutes at room temperature until its color changed to reddish brown Then, the flask was sealed and mixture was boiled at 100 °C for 2

hours until slurry was formed and the color changed to bright yellow Then 15 ml of water was added followed by the addition of 30% H_2O_2 (4-5 ml) and stirred for 30 minutes at room temperature. The solution was allowed to settle down and upper clear half was decanted After that, 20 ml of HCl and 50-60 ml of H_2O was added into the mixture and was stirred for 30 minutes and room temperature and again decanted until pH reached to 7 The Graphene oxide was filtered and dried

3.2.3. Synthesis of TEOS functionalized Graphene oxide

200 mg of GO powder and 120 mL of ethanol were added in a flask and sonicated for 1 hour to form a homogenous solution The pH of the solution was adjusted to about 3-4 with 10% HCl solution. 20 ml of ethanol and 0 6 g of TEOS (666 µl) was mixed uniformly and added slowly into GO solution After, 12 hr sonication at 60°C, the product was washed with ethanol many times until all the unreacted TEOS was removed and then it was dried (Li et al , 2015) The schematic flow diagram of TEOS functionalized Graphene Oxide is given in figure 1

3.2.4 Synthesis of carrageenan/Graphene oxide nanocomposite

In the synthesis of carrageenan/Graphene oxide nanocomposite 1g carrageenan powder was dissolved in 30 ml distilled water at 80°C temperature for 1 hour and 0 01g functionalized GO (f-GO) was sonicated for 18 hours After complete dissolution of carrageenan, the sonicated f-GO was added drop by drop into the carrageenan solution It was allowed to stir for an hour After stirring, the solution was again sonicated for an hour The carrageenan/f-GO solution was poured into the syringe and was allowed to drop into the ethanol Then 100 µl 11 OS was added drop by drop in the beads. The beads were poured into dishes and then were allowed to dry for 2 days The schematic flow diagram is given in figure 2

3.3. Characterization Techniques

Following techniques were used to characterize the synthesized beads

3.3.1. FT-IR Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is a technique used to analyze the structure of the composite FTIR spectra were obtained using a Nicolet 8700 FTIR spectrometer

(Thermo Scientific Instrument) using germanium crystal The IR spectra were obtained at the resolution of 6 cm^{-1} from 500-4000 cm^{-1} (Bibi et al , 2015)

3.3.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used to study the thermal behavior of the composites formed The thermogravimetric analysis was performed a Mettler Toledo, TGA/DSC star system under nitrogen flow (50mL/min) Experiments were carried out at a heating rate of 20 °C/min from 80 °C up to a maximum of 675 °C (Kamal et al , 2016)

3.3.3. Raman Spectroscopy

Raman spectroscopy is widely used to characterize crystal structure, disorder and defects in graphene-based materials Raman spectra were taken at room temperature under ambient conditions using Renishaw in Via Raman microscope with 532 nm (Diode pump solid DPSS) green laser. Charged couple device detector was used to obtain the Raman spectra (Bibi et al , 2015)

3.3.4. Scanning Electron Microscope (SEM)

The results of SEM were observed using a JEOL, JSM-6400 scanning microscope Bruker silicon drift EDS detector coupled with the SEM was used to investigate the chemical nature of the samples The samples were analyzed at different magnifications (Bibi et al , 2015)

3.4. Experimental

3.4.1. Swelling measurements

Dried carrageenan beads were used to determine the degree of swelling Gravimetric method was used to study the swelling behavior of carrageenan beads The percentage degree of swelling (% DS) was determined by immersing the beads (0.5 g) in distilled water and allowed to soak at room temperature for 24 h Then, they were removed and blotted with filter paper to remove surface water, weighed and the % DS was calculated using

$$\% DS = \frac{Ws - Wd}{Ws} \times 100$$

Where W_s and W_d are the weights of the samples swollen in water and in dry state, respectively (Mahdavinia et al, 2014)

3.4.2. Preparation of stock solution

0 01 g of Crystal Violet dye was dissolved in 1 L of deionized water to prepare the stock solution of 100 mg/L The other solutions were successively dilluted with different concentrations The pH of the stock solution was adjusted by using 1 0 mol/L HCl or 1 0 mol/L NaOH (Yan et al, 2014)

3.4.3. Dye adsorption

Dye adsorption was carried out by immersing 0 05 g of beads into 10mL of dye solution with 10 mg L^{-1} of CV All adsorption experiments were examined through a batch method on a shaker with a constant speed at 140 rpm To study the adsorption kinetics, at specified time intervals, the amount of adsorbed CV was evaluated using a UV spectrometer (UV-1201 UV-VIS-Spectrophotometer, SHIMADZU) at λ_{max} = 590 nm The content of adsorbed dye was calculated as

$$qt = \frac{Co - Ct}{m} \times V$$

Where, C_o is the initial CV concentration (mg L^{-1}), C_t is the remaining dye concentration in the solution at time t, V is the volume of dye solution used (L), and m is the weight of beads (g) Adsorption isotherm was carried out by immersing 0 05 g of the beads into 10 mL of dye solutions with 10,20,30,40,50,60,70 and 80 mg L^{-1} of CV The equilibrium adsorption capacity of nanocomposites, qe (mg g^{-1}), was determined using above mentioned equation In this equation, the Ct and the qt are replaced with equilibrium concentration of dye in solution (Ce) and equilibrium adsorption capacity (qe), respectively (Mahdavinia et al, 2014)

To evaluate the effect of pH on the adsorption capacity of beads, the pH of initial dye solutions was adjusted by adding dilute HCl and NaOH solutions
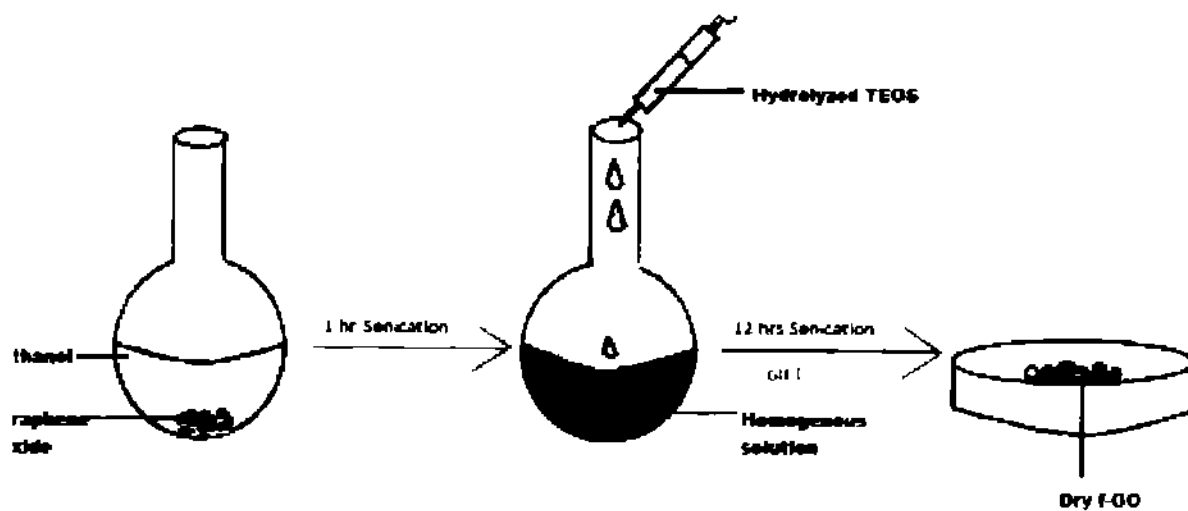
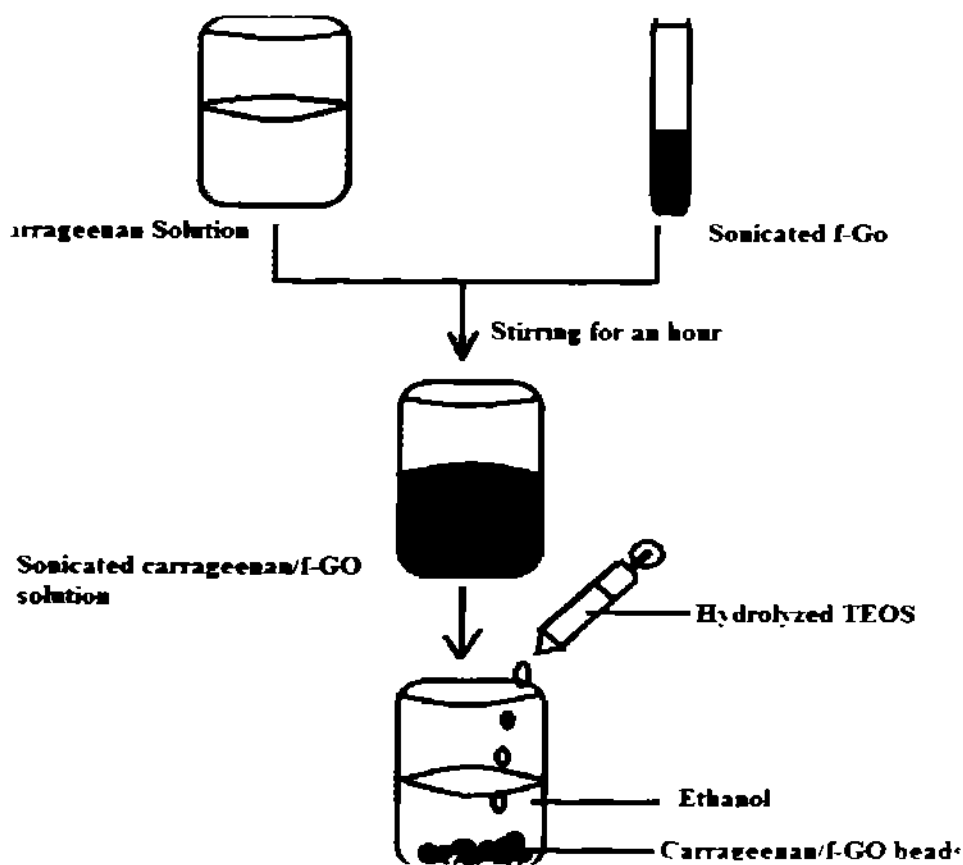**Figure: 7. Silane functionalization of Graphene**

Figure: 8. Synthesis of carrageenan/f-GO composite

3.4.4. Adsorption kinetics

Adsorption kinetics as a useful information on the rate of dye adsorption can be considered as an important factor for proper design of adsorbent (Liu & Zhang, 2007) The effect of contact time on the adsorption of crystal violet on beads was investigated The experimental kinetic data were analyzed by pseudo- first- order and pseudo-second-order models The pseudo-first- order equation is described as below (Dai et al , 2011)

$$Ln(qe - qt) = Lnqe1 - k1t$$

Where qe and qt (mg g^{-1}) are the amounts of adsorbed dye on the beads at equilibrium and at time t, respectively qe1 and k1 (min^{-1}) show the theoretical equilibrium adsorption and rate constant of pseudo-first-order kinetic, respectively

Also, kinetic data were analyzed using the pseudo-second- order model (Dai et al 2011)

$$\frac{1}{qt} = \frac{1}{k2qe2} + \frac{t}{qe2}$$

Where k2 (g mg^{-1} min^{-1}) is rate constant of pseudo-second- order kinetic and qe2 is the theoretical adsorbed dye (mg g^{-1})

3.5. Statistical Analysis

The adsorption parameters such as contact time, pH, concentration of adsorbate and amount of adsorbent were also observed by mean and standard deviation

RESULTS AND DISCUSSION

4.1. Synthesis and characterization

The crosslinked carrageenan beads were prepared by ex-situ crosslinking of carrageenan beads FT-IR results show the successful interaction of polymer chains of carrageenan with silane groups of TEOS The partial positive charge of silane interacts with the sulphate group of carrageenan polymer chains and thus leading to successful crosslinking of carrageenan beads Figure 1 and 2 shows the schematic mechanism of crosslinking of carrageenan beads and CG/f-GO beads respectively
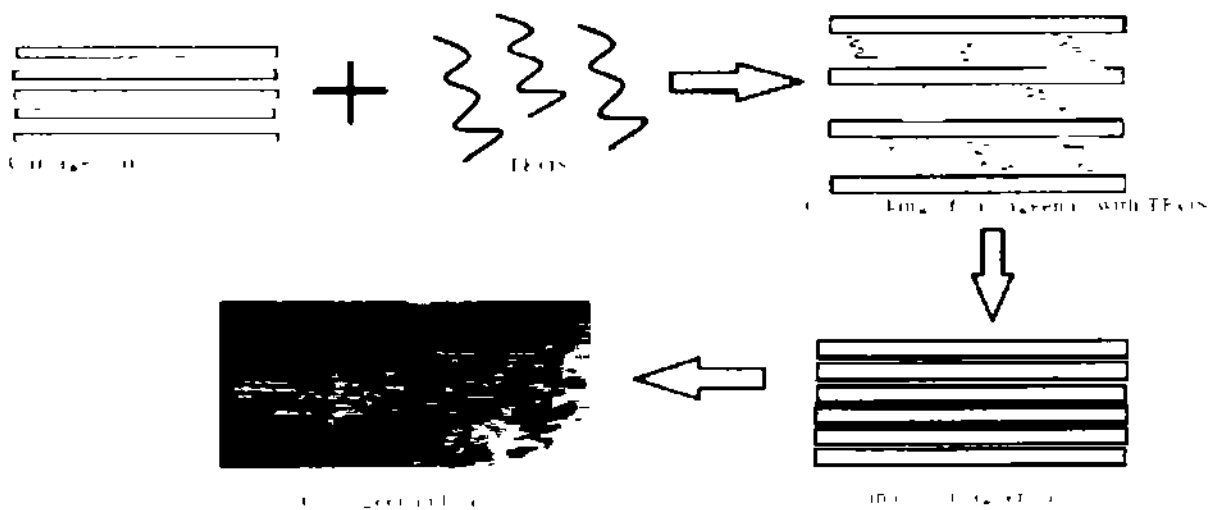

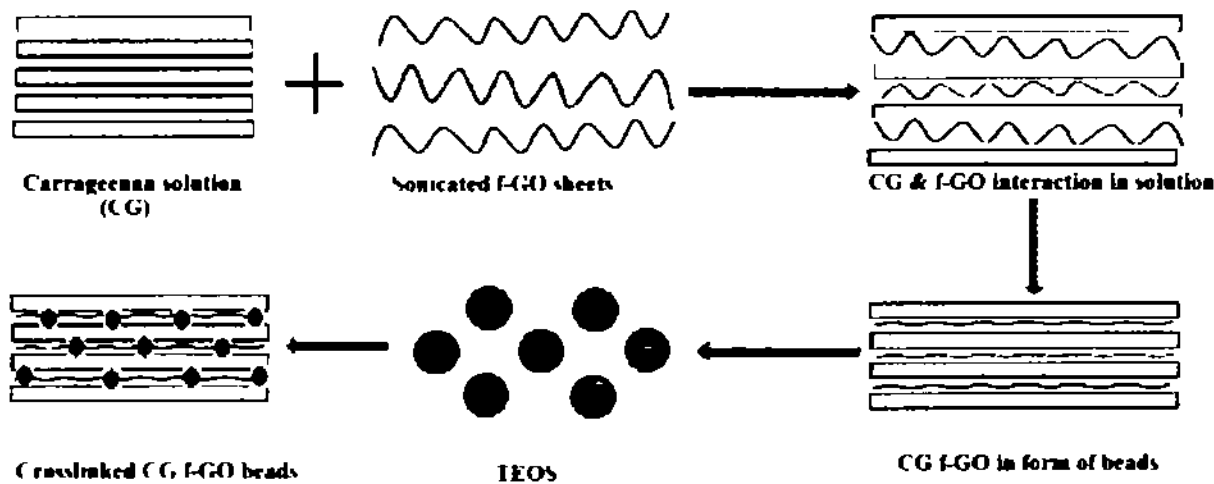**Figure.1. Schematic mechanism of synthesis of carrageenan beads**

Figure.2. Schematic mechanism of synthesis of CG/f-GO beads

4.1 Characterization Study

4.1.1. FT-IR spectra

The FT-IR spectra of pristine carrageenan powder are shown in figure 1 Carrageenan exhibited characteristic peaks at 3255 cm^{-1} and 3393 cm^{-1} which are due to O-H stretching The appeared at 2935 cm^{-1} correspond to C-H stretching vibration of alkane groups in the carrageenan polymer chain A peak at 1219 cm^{-1} is attributed to sulphate ester groups of carrageenan A peak observed at 926 cm^{-1} corresponds to the 3-6 anhydro- D -galactose and a characteristic peak observed at 842 cm^{-1} is due to presence of galactose-4-sulphate group Similar results were analyzed by Mahadivima et al , 2015 in the study kappa-Carrageenan beads as new adsorbent to remove crystal violet dye from water. adsorption kinetics and isotherm

Figure 2 indicates the FTIR spectrum of carrageenan beads without crosslinking (Q_0) and carrageenan beads after crosslinking with 1200μl TEOS (Q_2) The spectrum of Q_0 beads shows the characteristic peaks at 2920 cm^{-1} and 2853cm^{-1} which indicates the presence of C-H stretch The Q_2 peak shifted towards left at 1622 cm^{-1} indicating the presence of stretching vibration of C=C of the unoxidized sp^2 CC bonds while the Q_0 peak at 1581 cm-1 indicates the presence of C-C stretch The Q_2 peak at 1030 cm^{-1} indicates the presence of Si-O-C linkage indicating the successful crosslinking of carrageenan beads The peaks at 925 cm^{-1} and 843 cm^{-1} are attributed to the 3,6 anhydro Galactose and α (1-3)-D-Galactose linkage which are present in both Q_0 and Q_2 beads

FT-IR spectra of GO and TEOS functionalized GO are presented in figure 3 The FTIR of GO shows that peak appeared at 1712 cm^{-1} is the characteristic bond of the C=O stretching mode of carboxylic groups of GO The band at 3687 cm^{-1} is attributed to stretching vibration of OH of hydroxyl group The appearance of band at 1616 cm^{-1} is assigned to the stretching vibration of C=C of the unoxidized sp^2 CC bonds The peak at 2354 cm^{-1} is corresponding to the stretching vibration of C-H group The peaks located at 3687, 1712, 1616 and 2354 cm^{-1} in the GO spectrum indicate the presence of OH, C=O and C-O stretch respectively which suggests the existence of hydroxyl, carboxyl and alkoxy groups on the surface of GO

After functionalization of GO with TEOS, the band at 3687 cm^{-1} became weaker and two new bands at 3062 cm^{-1} and 2972 cm^{-1} appear corresponding to the stretching of $-CH_2$ groups from alkyl chains assigning to the silane moieties of silane functionalized GO The appearance of band at 1028 cm^{-1} is assigned to the Si-O-C bonds, indicating the successful functionalization of GO Similar results were found by Yan et al , 2014 in the study "Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide"

4.1.2. Thermo gravimetric analysis (TGA)

TGA analysis was conducted to test the thermal stability of GO sheet Results were shown in Figure 4 Three stages were observed in the quality loss cure of the GO sheet Firstly, a roughly 5% quality loss occurred at the temperature of 100°C, primarily due to the loss of H_2O molecules in the GO sheet layers Secondly, the thermal decomposition of instable oxygen-containing functional groups showed a roughly 15% quality loss, occurring at a temperature of 250°C Finally, a 68% quality loss occurred at 500°C was mainly due to the combustion of the carbon skeleton

4.3.4. Raman spectroscopy

Raman spectroscopy is widely used to characterize crystal structure disorder and defects in graphene-based materials [Guoa et al , 2012] Raman spectra were taken at room temperature under ambient conditions using Renishaw inVia Raman microscope with 532 nm (Diode pump solid, DPSS) green laser Charged couple device detector was used to obtain the Raman spectra of GO Figure 5 shows D peak of GO located at 1346 cm^{-1}, the G peak at around 1603 cm^{-1} and 2D peak at 2952 cm^{-1} Similar results were found by Childres et al , in "Raman spectroscopy of graphene and related materials" showing peak of D-band at 1350 cm-^{1} G-band at 1580 cm^{-1} and 2D band at 2690 cm^{-1}

4.3.5. SEM Analysis of GO

Figure 6 shows SEM images of GO and chemically reduced GO Single flakes of GO may be observed Graphene oxide flakes have relatively large surface (with the edge of sheets about the size of micrometers) and its morphology resembles thin curtain These parameters indicate very good exfoliation of graphite during oxidation process
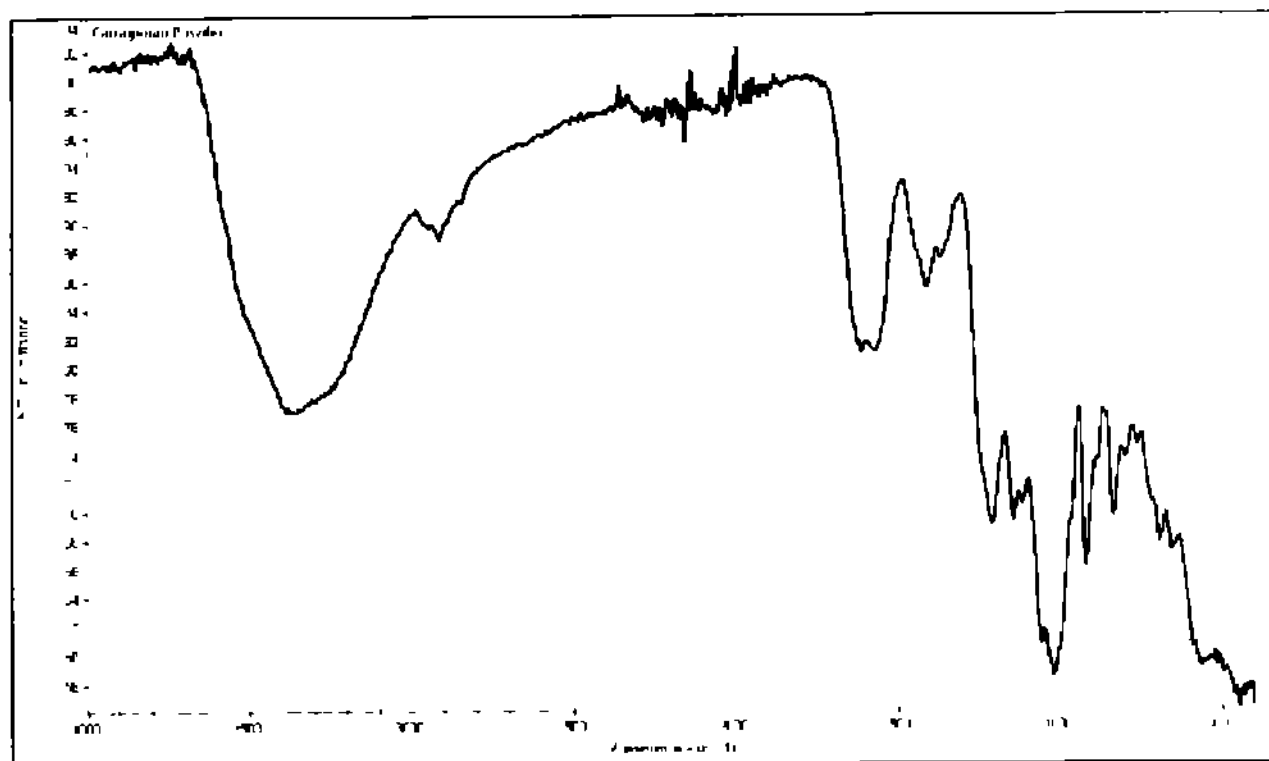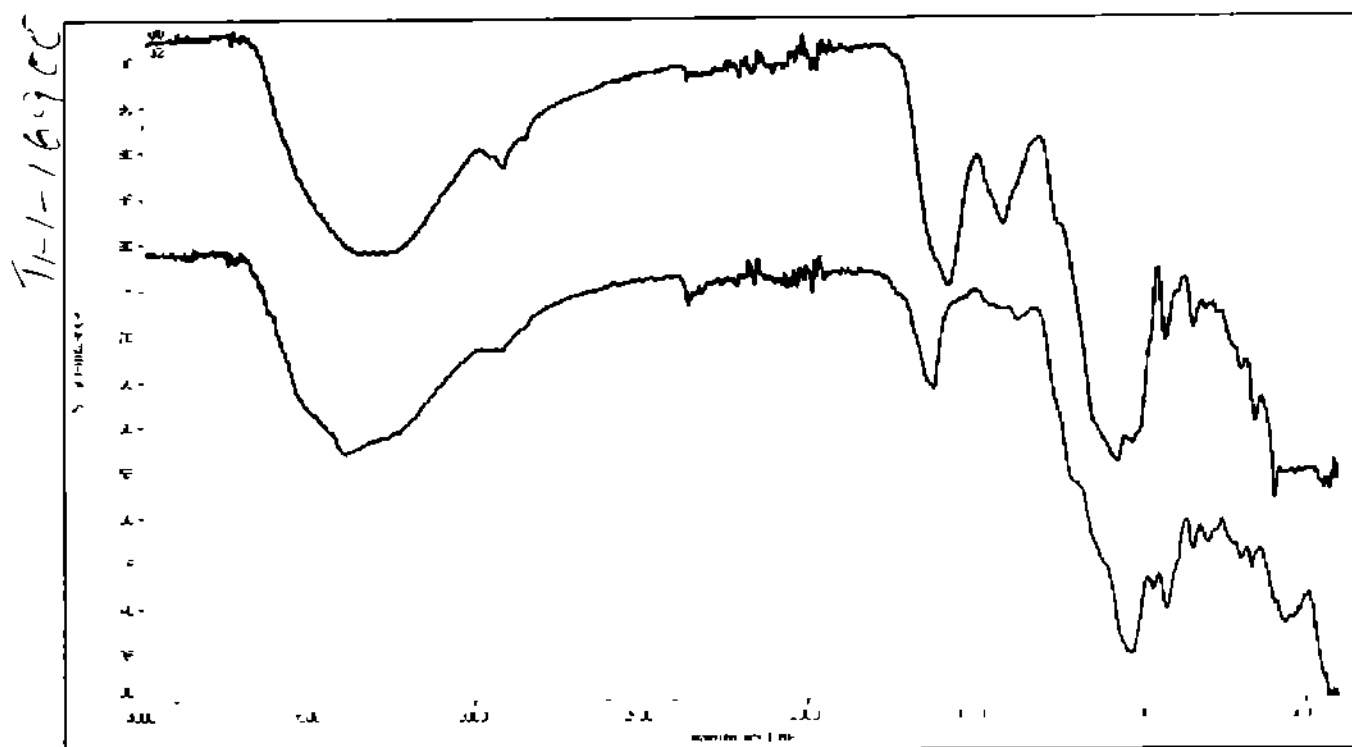
Figure: 9. FTIR spectra of carrageenan powder

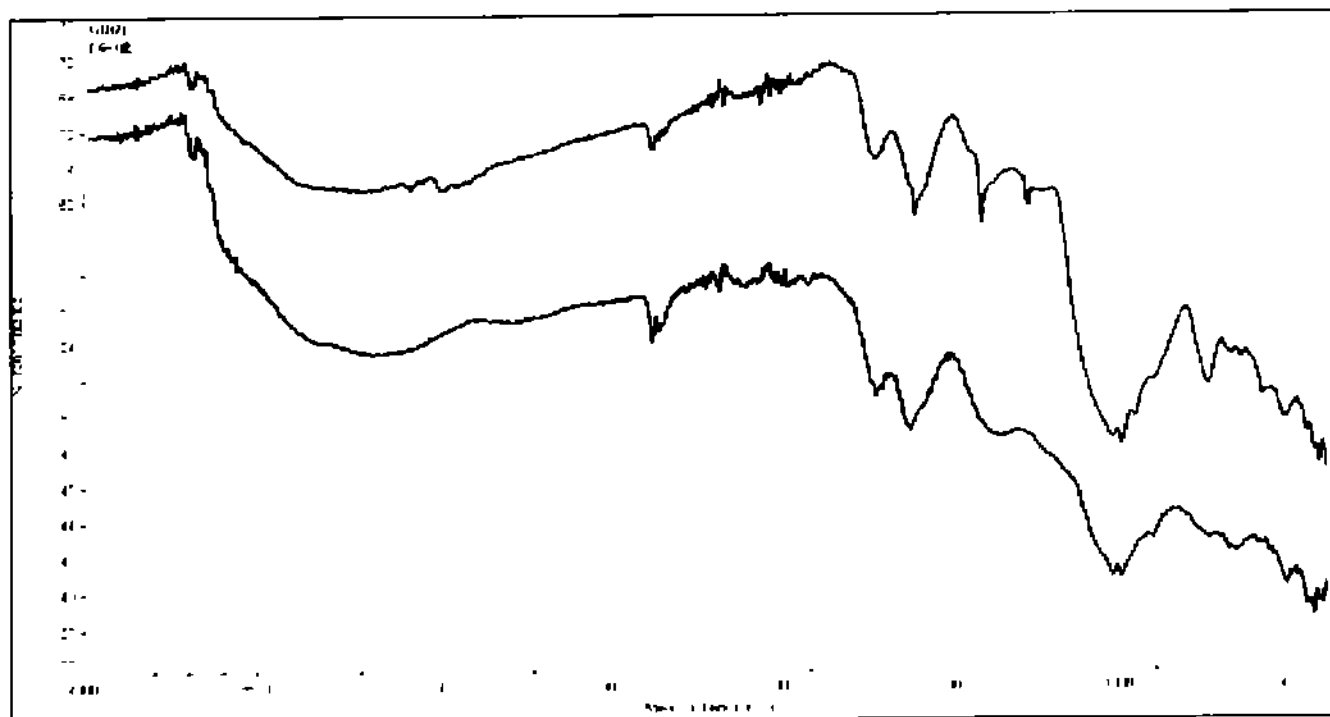Figure: 10. FTIR spectra of Q₀ and Q₂ beads
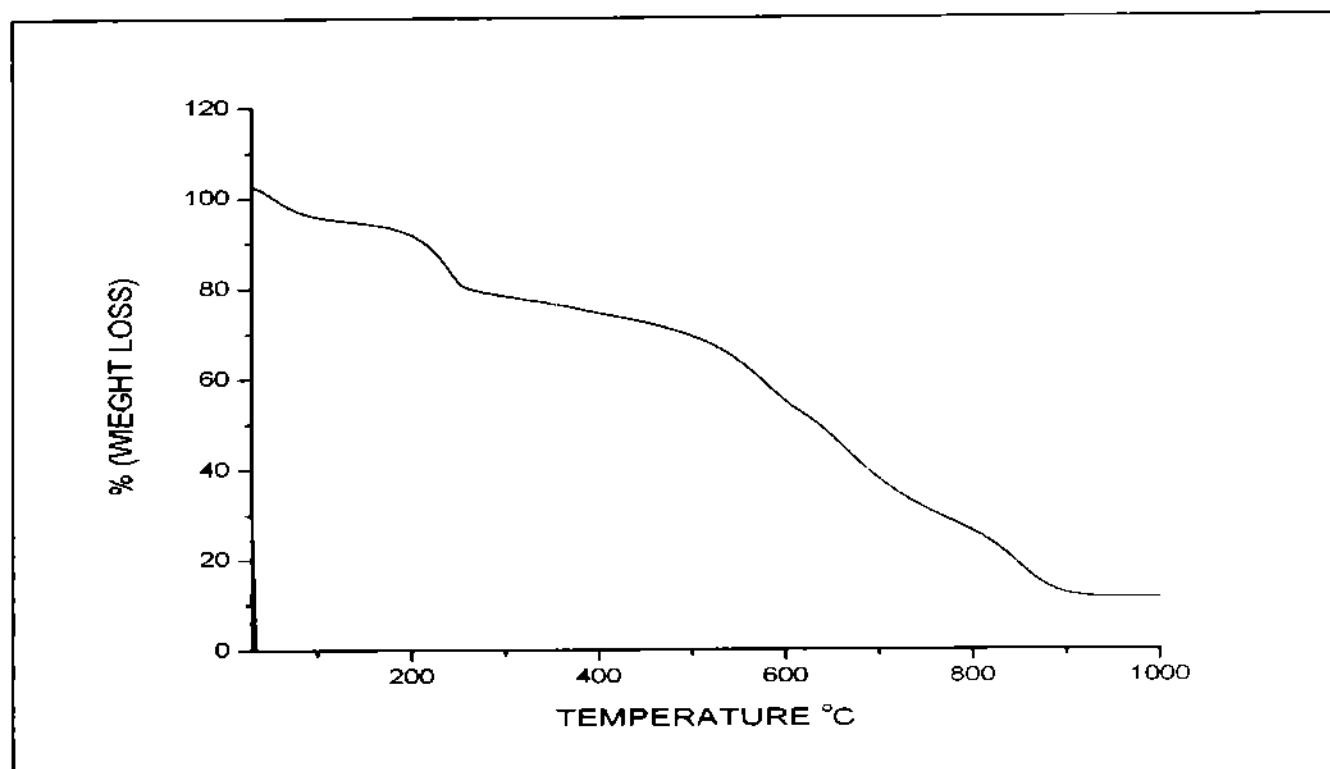
Figure: 11. FTIR spectra of GO and f-GO
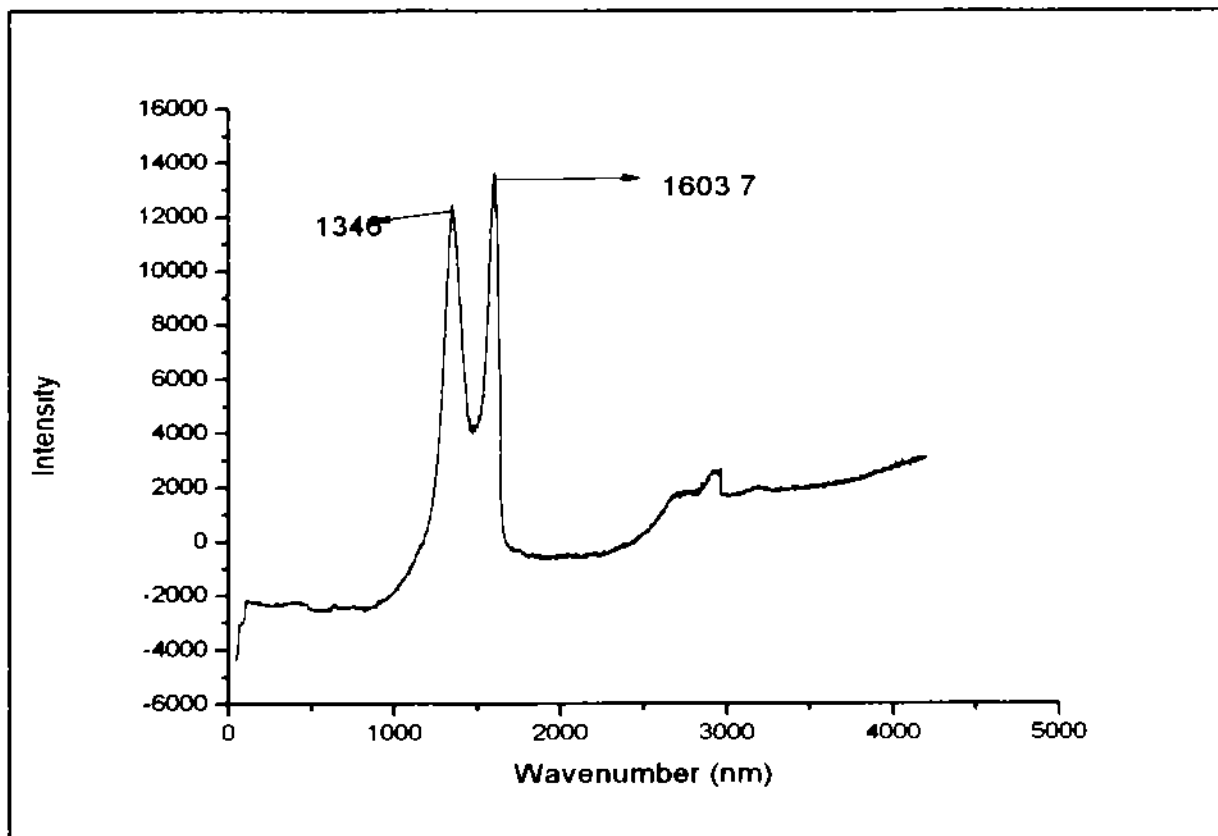
Figure: 12. TGA of GO
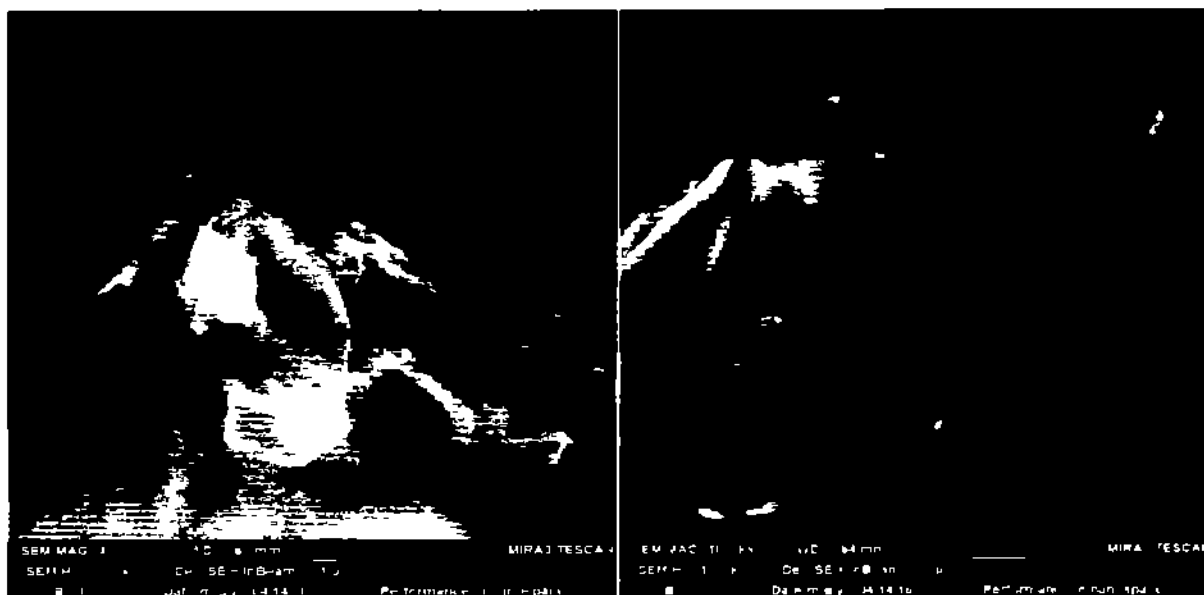
Figure: 13. Raman spectra of GO

Figure: 14. SEM of GO

4.4. Swelling study

The behavior of swelling was determined by soaking the carrageenan beads in deionized water The degree of swelling mainly depends upon the chemical composition, degree of crosslinking and affinity of water The degree of swelling was found 39 39 % The rigid structure of carrageenan beads restricts its expansion to uptake water Such a behavior of carrageenan beads can be attributed to strong interaction of sulphate groups and increased degree of crosslinking and thus leading to reduced water absorbency(Mahdavinia *et al* . 2014)

4.5. Adsorption study

4.3.1. Effect of pH on adsorption

The pH of aqueous solutions affects the removal efficiency of adsorbate by altering the structure and surface of active sites of the substrate adsorbent Figure 7 shows the results of adsorbent removal efficiency with different pH value of solution It was found that carrageenan beads showed maximum dye removal (17%) at pH 7 The ionic pendants are completely dissociated at pH 7 In acidic medium, it also adsorbs crystal violet probably due to increased interaction of sulphate group with the cationic dye while in basic environment the removal efficiency decreases and it may attributed to OH- screening effect on sulphate groups Mahadivinia *et al*, 2015) Because of this behavior, the synthesized carrageenan beads are considered to be an efficient adsorbent to remove crystal violet dye in acidic and neutral pH

4.3.2. Effect of adsorbate concentration

The adsorption of CV onto beads was examined with change in initial dye concentration by immersing the beads in solutions with concentrations ranging from 10-140 mgL ^{1} Results shows that by increasing the CV concentration in the dye solutions the rate of adsorption by beads was increased and then reached the maximum level at 140 mgL ^{1} (Figure 8) This indicates that all the active sites on the beads have been occupied and became saturated and capacity remains constant (Mahadivinia *et al*, 2015)

Soedjak, H S (1994) Colorimetric determination of carrageenans and other anionic hydrocolloids with methylene blue *Analytical Chemistry, 66* 4514-4518

Strickland, A F, & Perkins, W S (1995) Decoloration of continuous dyeing wastewater by ozonation *Textile Chemist and Colorist, 27,* 5-11

Thrimawithana, T R, Young, S, Dunstan, D E, & Alany, R G (2010) Texture and rheological characterization of kappa and iota carrageenan in the presence of counter ions *Carbohydrate Polymers, 82,* 69-77

Udaybhaskar, P, Iyengar, L, & Rao, A V S A (1990) Hexavalent chromium interaction with chitosan *Applied Polymer Science, 39,* 739-747

Vasconcelos, L A T d, & Beça, C G G (1994) Adsorption equilibria between pine bark and several ions in aqueous solution, Pb(II) *European Water Pollution Control 4* 41-51

Verma, A K, Dash, R R, & Bhunia, P (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters *Journal of Environmental Management, 93,* 154-168

Wan, Y -J, Gong, L -X, Tang, L -C, Wu, L -B, & Jiang, J -X (2014) Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide *Composites Part I 64* 79-89

Yan, Y, Wen-Qin, W, Hai-Hau, Z, Zhong-Yuan, H, Ting-Ting, Y, Rui, L, & Ya-Fei, K (2014) Adsorption behavior of cross-linked chitosan modified by graphene oxide for Cu (II) removal *Journal of Central South University of Technology 21* 2826 2831

Yang, X, Tu, Y, Li, L, Shang, S, & Tao, X -m (2010) Well-Dispersed Chitosan Graphene Oxide Nanocomposites *ACS Applied Materials Interfaces. 6* 1707-1713

Yermak, I M, Kim, Y H, Titlynov, E A, Isakov, V V, & Solov'eva, I I (1999) Chemical structure and gel properties of carrageenans from algae belonging to the Gigartinaceae and Tichocarpaceae, collected from the Russian Pacific coast *Journal of Applied Phycology, 11,* 41-48

Zhao, G, Li, J, Ren, X, Chen, C, & Wang, X (2011) Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management *Environmental Science Technology, 45,* 10454-10462

Removal efficiency (%) at different pH

Removal efficiency at different concentrations of crystal violet dye
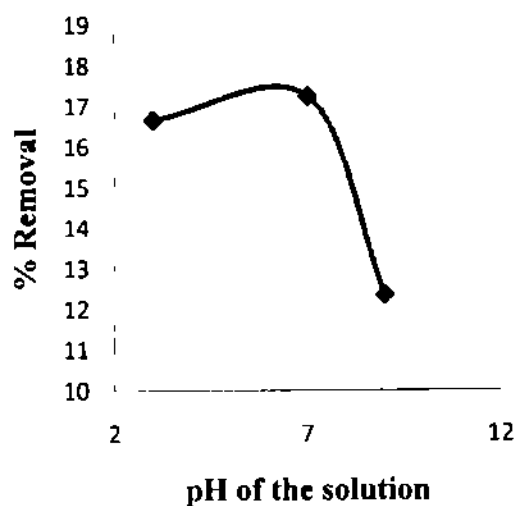
Figure: 15. RE at different pHs
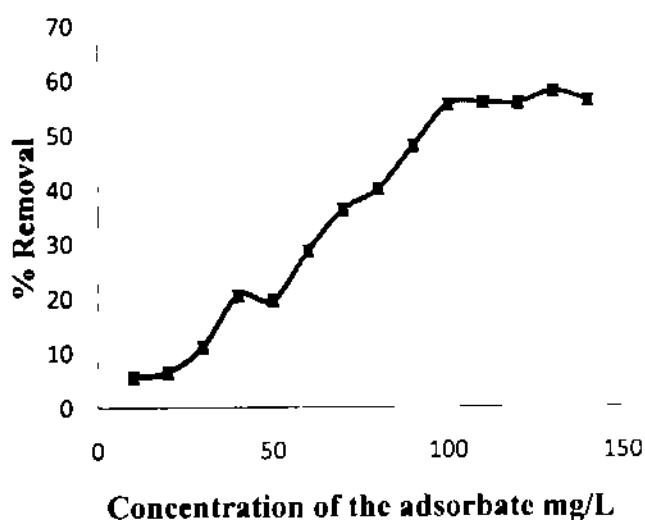
Figure: 16. RE at different concentrations

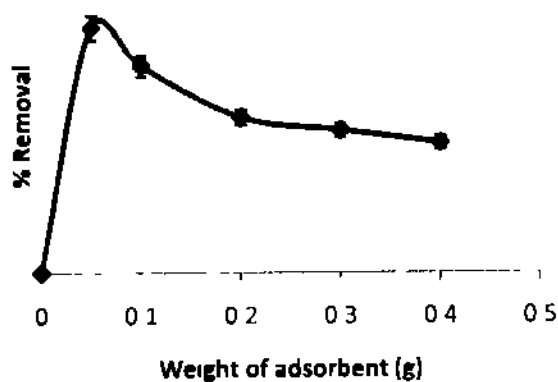**% Removal at different adsorbent dosage**

Pseudo-first-order Model

$R^2 = 0.015$

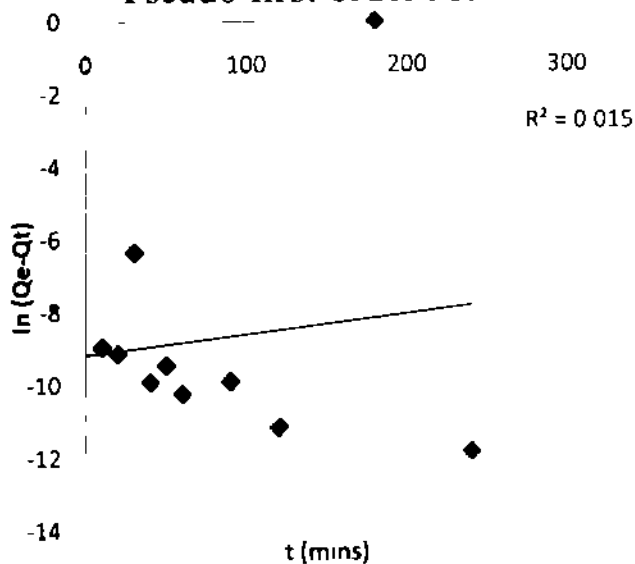Figure: 17. RE at different adsorbent dosage

Figure: 18. Pseudo-first-order Model

4.3.3. Effect of adsorbent dose

The effect of substrate (adsorbent) dose on the adsorption level of CV dye is studied and results are shown in figure 9 The amount of adsorbent varied from 0 05 to 0 4 g and maximum adsorption of CV dye was obtained at 0 05 g of beads At a particular weight of 0 05 g the removal efficiency by carrageenan beads began to level off This behavior depicts that with increase in the adsorbent amount there is an increase in the instauration sites of adsorbent i e all the active sites of carrageenan beads are occupied by CV dye particles (Mahadivinia *et al*. 2015)

4.3.4. Adsorption Kinetics

The kinetic of adsorption is one of the many factors which represents the pollutant adsorption rate and away to find the adsorption efficiency Hence, the contact time period of beads and CV dye is an important factor to determine the adsorption rate Batch method was used to examine the effect of contact time. The beads were immersed into 10 mgL^{-1} of CV dye solution at 35°C. The removal rate of dye was increased in first 10 minutes then reached at constant level and maintained the equilibrium level All the active sites of carrageenan beads occupied by CV in first 10 minutes and became saturated The rate constant and equilibrium adsorption capacity of carrageenan beads were statistically analyzed by pseudo-first-order Model and pseudo-second-order Model The kinetic data was analyzed by pseudo-first-order model as

$$Ln(qe - qt) = Lnqe1 - k1t$$

Pseudo-second-order model was also applied to examine the kinetic data by following equation

$$\frac{1}{qt} = \frac{1}{k2qe2} + \frac{t}{qe2}$$

It is represented in figure 10, data is not fitting best in pseudo-first-order model It best fits pseudo-second-order model as seen in figure 11 It was found that plot of t/Qt against t gives a high correlation coefficient with $R^2 > 0$ 999 which depicts the best fitting of pseudo-second-order model According to pseudo-second-order kinetics, the theoretical equilibrium adsorption capacities are in agreement with the experimental data The adsorption takes place through

various steps like surface diffusion, pore diffusion or by adsorption on the pore surface at sufficient stirring speed The graph between Qt and $t^{0.5}$ shows that the intra-particle diffusion is not a rate limiting step of adsorption kinetics as it is not passing through a straight line (figure 12)

Pseudo-second-order Model

$R^2 = 0.999$

y-axis: t/Qt (min g/mg)
x-axis: t (mins)
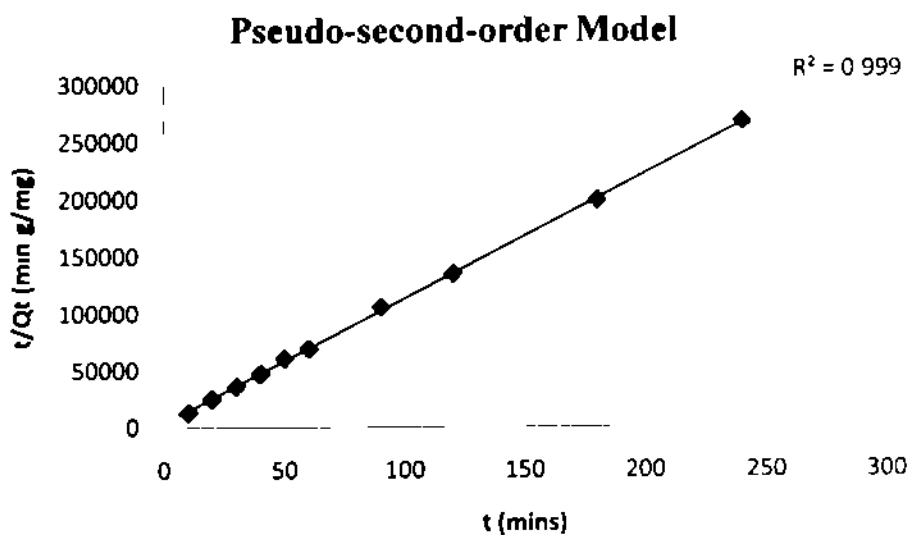
Figure: 19. Pseudo-second-order Model

Intraparticle diffusion Model

$y = 1E-05x \quad 0.000$
$R^2 - 0.815$

y-axis: Qt (mg/g)
x-axis: t^ (mins)
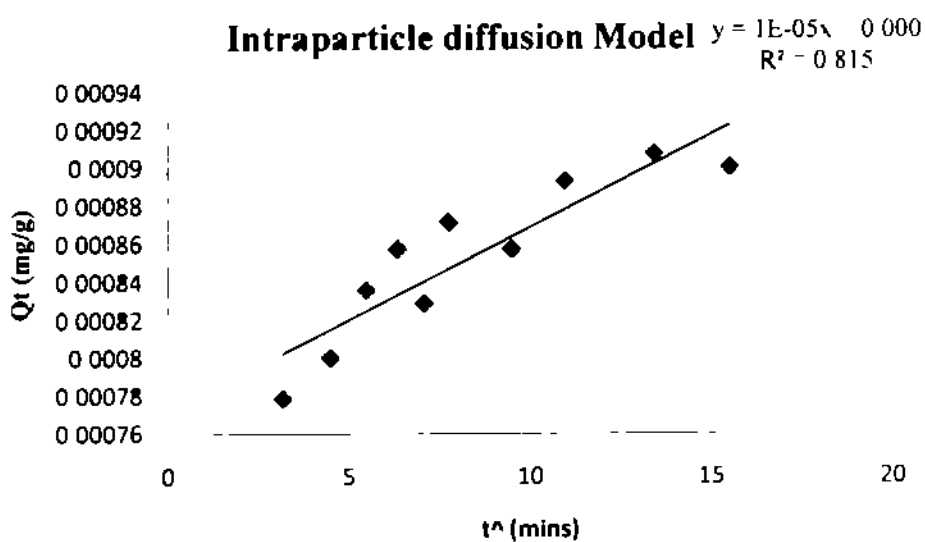
Figure: 20. Intraparticle diffusion Model

CONCLUSION

Conclusion:

The crosslinked carrageenan beads and carrageenan/ graphene oxide nanocomposite was synthesized by exsitu crosslinking method and achieved stability in water. Crosslinked carrageenan beads were evaluated to remove CV from aqueous solutions. The synthesized crosslinked carrageenan beads were found efficient for the adsorption of crystal violet dye from aqueous solutions. The results depicted that it can absorb CV in very less time i e 10 minutes. The effect of pH on the adsorption capacity of beads was studied and it was found that it can behave efficiently in acidic and neutral environment. The adsorption capacity of carrageenan beads was also determined by varying the adsorbent dosage and maximum adsorption was achieved in lowest adsorbent dosage. The adsorption kinetics of dye was also analyzed by pseudo-first-order model and pseudo-second-order model and pseudo-second-order model was obtained best to fit experimental data. The effect of concentration of CV dye revealed that the adsorption capacity of beads for CV was efficient to remove maximum concentration of CV up to 140 mg g^{-1}. According to above described results, it was found that carrageenan is an efficient to remove cationic dye such as CV in lesser time with low adsorbent dosage.

REFERENCES:

Adak, A.. Bandyopadhyay, M , & Pal, A. (2005) Removal of crystal violet dye from wastewater by surfactant-modified alumina *Separation and Purification Technology* 44, 139-144

Ahmad, R (2009) Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP) *Journal of Hazardous Materials* 171 767-773

Aksu, Z (2005) Application of biosorption for the removal of organic pollutants a review *Process Biochemistry*, 40, 997-1026

Bhatnagar, A , & Jain, A K (2005) A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water *Journal of Colloid and Interface Science* 281, 49-55

Bibi, S , Yasin, T , Hassan, S , Riaz, M , & Nawaz, M (2015) Chitosan/CNTs green nanocomposite membrane Synthesis, swelling and polyaromatic hydrocarbons removal *Materials Science and Engineering*, 46, 359-365

Billiet, T , Vandenhaute, M , Schelfhout, J , Vlierberghe, S V , & P Dubruel (2012) A review of trends and limitations in hydrogel-rapid prototyping for tissue engineering *Biomaterials*, 33 6020-6041

Campo, V L , Kawano, D F , Jr, D B d S , & Carvalho, I (2009) Carrageenans Biological properties, chemical modifications and structural analysis - A review *Carbohydrate Polymers*, 77 167-180

Campo, V L , Kawano, D F , Jr Silva, D. B , & Carvalho, D I (2009) Carrageenans Biological properties, chemical modifications and structural analysis-A review *Carbohydrate Polymers*, 77, 167-180

Chakraborty, S , Chowdhury, S , & Saha, P D (2011) Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk *Carbohydrate Polymers*, 86 1533-1541

Chatterjee, S , Lee, M. W , & Wooa, S H (2010) Adsorption of congo red by chitosan hydrogel beads impregnated with carbon nanotubes *Bioresource Technology*, 101 1800-1806

Crini, G. (2006) Non-conventional low-cost adsorbents for dye removal A review *Bioresource Technology*, 97, 1061-1085

Crini, G g (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment *Progress in Polymer Science*, 30 38-70

Dai, J, Yang, H, Yan, H, Shangguan, Y, Zheng, Q, & Cheng, R (2011) Phosphate adsorption from aqueous solutions by disused adsorbents chitosan hydrogel beads after the removal of copper (II) *Chemical Engineering Journal 166,* 970-977

Daniel-da-Silva, A L, Lóiob, R, Lopes-da-Silva, J A, Trindade, I, Goodfellowa, B J, & Gil, A M (2008) Effects of magnetite nanoparticles on the thermorheological properties of carrageenan hydrogels *Journal of Colloid and Interface Science, 324* 205-211

Demirbas, A (2009) Agricultural based activated carbons for the removal of dyes from aqueous solutions A review *Journal of Hazardous Materials, 167,* 1-9

Dil, D A S, Qazi, P D I A, Baig, D M A, Khan, D E A, & Tahir, D A (2008) National Standards for Drinking Water Quality (pp. 3-8) Pakistan Pakistan Environmental Protection Agency

Forgacs, E, Cserha'ti, T, & Oros, G (2004) Removal of synthetic dyes from wastewaters a review *Environment International, 30,* 953 - 971

Ghanam, D, & Kleinebudde, P (2011) Suitability of kappa-carrageenan pellets forthe formulation of multiparticulate tablets with modified release *International Journal of Pharmaceutics, 409,* 9-18

Irfan, M (2009) Wastewater Treatment in Textile, Tanneries and Electroplating Industries especially by Activated Sludge Method- A technical report *Journal of Pakistan Institute of Chemical Engineers, 37,* 35-50

Jaina, R, Mathura, M, Sikarwara, S, & Mittal, A (2007) Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments *Journal of Environmental Management, 85,* 956-964

Jha, I N, Iyengar, L, & Rao, A V S P (1988) Removal of cadmium using chitosan *Journal of Environmental Engineering ASCE, 114,* 962-974

Kamal, M A, Yasin, T., Reinert, L, & Duclaux, L (2016) Adsorptive removal of copper (II) ions from aqueous solution by silane cross-linked chitosan/PVA/TEOS beads kinetics and isotherms *Desalination and Water Treatment, 57,* 4037-4048

Kazi, T G, Arain, M B, Jamali, M K, Jalbani, N, Afridi, H I, Sarfraz, R A, Shah, A Q (2009). Assessment of water quality of polluted lake using multivariate statistical techniques A case study *Ecotoxicology and Environmental Safety, 72,* 301- 309

Khattri, S D, & Singh, M K (1998) Color removal from aqueous solutions by adsorption *5* 230-234

Khattri, S D, & Singh, M K (2000). Colour removal from synthetic dye wastewater using a biosorbent *Water Air Soil Pollution, 120,* 283-294

Krolow, M Z , Hartwig, C A , Link, G C , Raubach, C W , Pereira, J S I . Picoloto. R S . Mesko, M. F (2011) Synthesis and Characterisation of Carbon Nanocomposites *Carbon Nanostructures*, 33-47

Li, L , Ni, R., Shao, Y., & Mao, S (2014) Carrageenan and its applications in drug delivery *Carbohydrate Polymers, 103*, 1- 11

Li, W , Zhou, B , Wang, M , Li, Z , & Ren, R (2015). Silane functionalization of graphene oxide and its use as a reinforcement in bismaleimide composites *Journal of Material Sciences 50*, 5402-5410

Lim, L B L , Priyantha, N , Zehra, T , Then, C. W . & Chan, C M (2016) Adsorption of crystal violet dye from aqueous solution onto chemically treated Artocarpus odoratissimus skin equilibrium, thermodynamics, and kinetics studies *Desalination and Water Treatment, 57*, 10246-10260.

Lima, L B L , Priyanth, N , Zehraa, T , Thena, C W., & Chan, C M (2016) Adsorption of crystal violet dye from aqueous solution onto chemically treated Artocarpus odoratissimus skin equilibrium, thermodynamics, and kinetics studies *Desalination and Water Treatment, 57*, 10246-10260

Liu, P , & Zhang, L (2007) Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents *Separation and Purification Technology, 58*, 32-39

Loryuenyong, V , Totepvimarn, K , Eimburanapravat, P , Boonchompoo, W . & Buasri A (2013) Preparation and Characterization of Reduced Graphene Oxide Sheets via Water-Based Exfoliation and Reduction Methods *Advances in Materials Science and Engineering, 6*, 1-5

Low, C K L K S . & Gan, P. Y (1999) Removal of some organic dyes by acid treat spent bleaching earth *Environmental Technology, 20* 99-104

Mahdavinia, G R , Bazmizeynabad, F , & Seyyedi, B (2015) kappa-Carrageenan beads as new adsorbent to remove crystal violet dye from water adsorption kinetics and isotherm *Desalination and Water Treatment, 53*, 2529-2539

Mahdavinia, G R , Iravani, S , Zoroufi, S , & Hosseinzadeh, H (2014) Magnetic and K'-cross-linked kappa-carrageenan nanocomposite beads and adsorption of crystal violet *Iran Polym Journal, 23*, 335-344

Mahdavinia, G R , Massoudi, A , Baghban, A , & Massoumi, B (2012) Novel carrageenan-based hydrogel nanocomposites containing laponite RD and their application to remove cationic dye *Iran Polymer Journal, 21*, 609-619

Mahdavinia, G R , & Mosallanezhad, A (2016) Facile and green rout to prepare magnetic and chitosan-crosslinked-k-carrageenan bionanocomposites for removal of methylene blue *Journal of Water Process Engineering, 10,* 143-155.

Masri, M S , Reuter, F W , & Friedman, M (1974) Binding of metal cations by natural substances *Applied Polymer Science, 18* 675-681

Mehmood, S J , Bi, F , Taj, N , Seema, Farhan, M , Shahid, M , Din, F U (2007) Physico-chemical Characterization of Carrageenan at different temperatures, isolated from *Hypnea musciformis* from Karachi coast, Pakistan *Journal of Applied Sciences, 7,* 3506-3511.

Mittal, A , Mittal, J , Malviya, A , D Kaur, & Gupta, V K (2010) Adsorption of hazardous crystal violet from wastewater by waste materials *Journal of Colloid and Interface Science, 343,* 463-473

Mittal, A , Mittal, J , Malviya, A , Kaur, D , & Gupta, V K (2010) Adsorption of hazardous dye crystal violet from wastewater by waste materials *Journal of Colloid and Interface Science, 343* 463-473

Mohammed, Y , Etonihu, A C , & Tsaku, V A (2011) Hexamethylpararosalinine chloride (crystal violet) oxidation by chlorate ions in aqueous acidic medium Kinetic approach to the mechanism of reaction *Trakia Journal of Sciences, 9,* 1-7

Nandi, B K , Goswami, A , Das, A K , Mondal, B , & Purkait, M K (2008) Kinetic and Equilibrium Studies on the Adsorption of Crystal Violet Dye using Kaolin as an Adsorbent *Separation Science and Technology, 43,* 1382-1403

Ngah, W S W , Sendud, C , & Mayanar, R (2002) Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads *Reactive and Functional Polymer 50,* 181-190

Ngaha, W S W , Teonga, L C , & Hanafiah, M A K M (2011) Adsorption of dyes and heavy metal ions by chitosan composites A review *Carbohydrate Polymers 83,* 1446-1456

Orhan, Y , & Buyukgüngor, H (1993). The removal of heavy metals by using agricultural wastes *Water Science and Technology, 28* 247-255

Paulchamy, B , Arthi, G , & Lignesh, B D (2015) A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial *Nanomedicine & Nanotechnology 6* 1-4

Pearcea, C I , Lloydb, J R , & Guthrie, J T (2003) The removal of colour from textile wastewater using whole bacterial cells a review *Dyes and Pigments, 58,* 179-196

Poots, V J P , McKay, G , & Healy, J J (1978) Removal of basic dye from effluent using wood as an adsorbent *Water Pollution Control Federation, 50,* 926-935

Prajapati, V D , Maheriya, P M , Jani, G K , & Solanki, H K (2014) Carrageenan A natural seaweed polysaccharide and its applications *Carbohydrate Polymers, 105* 97-112

Ramakrishnan, M , & Nagarajan, S (2009) Utilization of waste biomass for the removal of basic dye from water *World Applied Science, 5* 114-121

Randall, J M , Bermann, R L , Garrett, V , & Waiss, A C (1974) Use of bark to remove heavy metal ions from waste solutions *Forest Products, 24.* 80-84

Robinson, T., Chandran, B , & Nigam, P (2002) Studies on desorption of individual textile dyes and a syntheticdye effluent from dye-adsorbed agricultural residues using solvents *Bioresource Technology, 84,* 299-301

Robinson, T , Mullan, G M , Marchant. R , & Nigam, P (2001) Remediation of dyes in textile effluent a critical review on current treatment technologies with a proposed alternative *Bioresource Technology, 77,* 247-255

Rosen, M J (2004) *Adsorption of Surface-Active Agents at Interfaces The Electrical Double Layer* (Third ed) John Wiley & Sons , New York, USA

Saeeda, A , Sharif, M , & Iqbal, M (2010) Application potential of grapefruit peel as dye sorbent Kinetics, equilibrium and mechanism of crystal violet adsorption *Journal of Hazardous Materials, 179* 564-572

Sagbas, S., Butun, S , & N Sahiner (2012) Modifiable chemically crosslinked poli (j-carrageenan) particles *Carbohydrate Polymer, 87,* 2718-2724

Sankalia, M G , Mashru, R C , A Sankalia, J , & Sutariya, V B (2006) Stability improvement of alpha-amylase entrapped in kappa-carrageenan beads Physicochemical characterization and optimization using composite index *International Journal of Pharmaceutics, 312* 1-14

Seow, T W , & Lim, C K (2016) Removal of Dye by Adsorption A Review *International Journal of Applied Engineering Research, 11,* 2675-2679

Site, A D. (2001) Factors Affecting Sorption of Organic Compounds in Natural Sorbent/Water Systems and Sorption Coefficients for Selected Pollutants A Review *Journal of Physical and Chemical Reference Data, 187,* 188-432

Sivamani, S , & Leena Grace, B (2009) Removal of Dyes from Wastewater using Adsorption - A Review *International Journal of BioSciences and Technology, 4.* 47-51

Slokar, Y M , & Marechal, A M L (1998) Methods of Decoloration of Textile Wastewaters *Dyes and Pigments, 37,* 335-356

Soedjak, H S (1994) Colorimetric determination of carrageenans and other anionic hydrocolloids with methylene blue *Analytical Chemistry, 66* 4514-4518

Strickland, A F., & Perkins, W S (1995) Decoloration of continuous dyeing wastewater by ozonation *Textile Chemist and Colorist, 27,* 5-11

Thrimawithana, T R, Young, S, Dunstan, D E, & Alany, R G (2010) Texture and rheological characterization of kappa and iota carrageenan in the presence of counter ions *Carbohydrate Polymers, 82,* 69-77

Udaybhaskar, P, Iyengar, L, & Rao, A V S A (1990) Hexavalent chromium interaction with chitosan *Applied Polymer Science, 39,* 739-747

Vasconcelos, L A T d, & Beça, C G G (1994) Adsorption equilibria between pine bark and several ions in aqueous solution, Pb(II) *European Water Pollution Control 4* 41-51

Verma, A K, Dash, R R., & Bhunia, P (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters *Journal of Environmental Management 93,* 154-168

Wan, Y -J, Gong, L -X, Tang, L -C, Wu, L -B, & Jiang, J -X (2014) Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide *Composites Part I 64* 79-89

Yan, Y, Wen-Qin, W, Hai-Hau, Z, Zhong-Yuan, H, Ting-Ting, Y Rui, L, & Ya-Fei, K (2014) Adsorption behavior of cross-linked chitosan modified by graphene oxide for Cu (II) removal *Journal of Central South University of Technology 21* 2826 2831

Yang, X, Tu, Y, Li, L, Shang, S, & Tao, X -m (2010) Well-Dispersed Chitosan Graphene Oxide Nanocomposites *ACS Applied Materials Interfaces, 6* 1707-1713

Yermak, I M, Kim, Y H, Titlynov, E A, Isakov, V V, & Solov eva I I (1999) Chemical structure and gel properties of carrageenans from algae belonging to the Gigartinaceae and Tichocarpaceae, collected from the Russian Pacific coast *Journal of Applied Phycology, 11,* 41-48

Zhao, G, Li, J, Ren, X, Chen, C, & Wang, X (2011) Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management *Environmental Science Technology, 45,* 10454-10462