TREATMENT OF PHENOL AND CRYSTAL VIOLET DYE FROM WASTEWATER USING BIOSILICA HYDROGEL NANOCOMPOSITES

EASHA TIR RAZIA

DEPARTMENT OF ENVIRONMENTAL SCIENCES

KINNAIRD COLLEGE FOR WOMEN, LAHORE

2021-2023

TREATMENT OF PHENOL AND CRYSTAL VIOLET DYE FROM WASTEWATER USING BIOSILICA HYDROGEL NANOCOMPOSITES

A THESIS SUBMITTED TO KINNAIRD COLLEGE FOR WOMEN IN FULFILLMENTS OF THE REQUIREMENTS FOR THE DEGREE OF

M.PHIL

IN

ENVIRONMENTAL SCIENCES

By

EASHA TIR RAZIA

DEPARTMENT OF ENVIRONMENTAL SCIENCES

KINNAIRD COLLEGE FOR WOMEN, LAHORE

2021-2023

KINNAIRD COLLEGE FOR WOMEN, LAHORE
OFFICE OF RESEARCH, INNOVATION & COMMERCIALIZATION

Thesis Approval Certificate

Date: 18-1-2024

I hereby recommend that the thesis prepared under my supervision by

Student Name: Easha-Tir-Razia

Session: (2021-2023)

Registration No: 00319PES004

Title: Treatment of Phenol and Crystal Violet Dye from Wastewater Using Biosilica Hydrogel Nanocomposites

be accepted in partial fulfillment of the requirements for the award of MPhil degree.

Examination Committee Members

1. Name: Dr. Faiza Hassan — Signature & Date: 18/01/24
2. Name: Dr Amber Fatima — Signature & Date: 18/1/24
3. Name: Dr Almas Hamid — Signature & Date: 18/1/24

Supervisor's Name: Dr Sadia Saif, Dr Farzana Bashir — Signature & Date: 18/1/24

Dr Almas Hamid
Head of Department (Name)

Signature & Date 18/1/24

COUNTERSIGNED

Date: 18/1/24

Director ORIC

RESEARCH COMPLETION CERTIFICATE

It is certified that Easha Tir Razia, student of M.Phil. (Session 2021-2023), **Department of Environmental Sciences,** has carried out this research work entitled **Treatment of Phenol and Crystal Violet Dye from Wastewater using Biosilica Hydrogel Nanocomposites** under my supervision. It is assumed that this research work is original and has not been published anywhere else.

All changes suggested by examiners during defense are incorporated in this final copy.

Sadia Saif

Dr. Sadia Saif Dated: 22-01-2024
Assistant Professor
Department of Environmental Sciences
Kinnaird College for Women Lahore

Farzana

Dr. Farzana Bashir (Co-supervisor)
PSO PCSIR, Lahore

almas Hamid

Dr. Almas Hamid
Head of Department
Department of Environmental Sciences
Kinnaird College for Women Lahore

ANTI-PLAGIARISM DECLARATION

We certify that this is our research work. The work has not, in whole or in a part, been presented elsewhere for assessment. Where material has been used from other sources, it has been properly acknowledged. The similarity index of the research report is ---**14%**---. If this statement is untrue and we are found guilty of plagiarism, punitive actions against us should be taken as per Kinnaird Anti Plagiarism Policy.

Easha Tir Razia

W21MPES004

M.Phil Environmental Sciences

Sadia Saif

Dr. Sadia Saif:

Supervisor

almas Hamid

Dr. Almas Hamid:

Head of Department

ACKNOWLEDGEMENTS

First and foremost, I express my profound gratitude to Allah Almighty for granting me the strength, courage, and confidence needed to successfully complete this research endeavor. I extend my thanks to Prof. Dr. Rukhsana David, the Principal of Kinnaird College for Women Lahore, and Dr. Nikhat Khan, the Vice Principal of Kinnaird College for Women, for providing me with essential facilities crucial for our research.

I appreciate the collaboration of esteemed Ms. Almas Hamid, our Head of Department, and extend thanks to her for her cooperation. I particularly want to convey our deepest appreciation and indebtedness to my supervisor, Dr. Sadia Saif, and co-supervisor Dr. Farzana Bashir (Principal Officer at Centre for Environmental Studies, PCSIR Complex) whose invaluable guidance and encouragement, played an indispensable role throughout my research journey. This thesis would not have been possible without her expert guidance.

I would like to acknowledge all the other teachers in the department for their encouragement and support. Special thanks to lab attendant for facilitating access to the necessary lab equipment.

Lastly, but most importantly, I am thankful to my Parents for their unwavering support. Gratitude is also extended to my siblings Yaqoot, Ahmer, Sadaf, Ali and friends for their constant belief in me and encouragement.

Thank You

Easha Tir Razia

ABSTRACT

In this study, adsorption of Phenol and Crystal Violet (CV) dye was investigated while using adsorbent Biosilica hydrogel nanocomposites. Biosilica hydrogel nanocomposites were prepared using the hydrogel extracted from okra mucilage and silica extracted from sugarcane bagasse. To examine the functional groups and morphology, these nanocomposites were characterized via Fourier Transform Infrared Radiations (FTIR), and Scanning Electron Microscope (SEM). The batch adsorption experiments were performed by varying factors such as pH, contact time, adsorbent dose and initial concentration. From the results it was found that the maximum removal of crystal violet was 83% at 0.1g/250mL, initial concentration 30 ppm, pH 12 and contact time of 30 minutes. Phenol showed the removal of 79% at optimum conditions i.e. dosage 0.4g/200mL, initial concentration 10 ppm, pH 7 and contact time of 15 minutes. Langmuir was best fitted for phenol (q_m 16.28 mg/g) while Freundlich (q_m 120.48 mg/g) for crystal violet. Hence, the results indicate that the biosilica hydrogel nanocomposites proved to be more effective for removal of crystal violet as compared to phenol. Moreover, the synthesized adsorbent can be used as the efficient and cost-effective alternative for the adsorption of toxic pollutants and coloring agents from wastewater.

Table of Contents

Title **Page.No.**

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Abbreviations	Full Form
APS	Ammonium Persulfate
CV	Crystal Violet
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
EU	European Union
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Radiations
GO	Graphene oxide
HCl	Hydrochloric acid
kC	kappa-carrageenan
MBA	N,N′-methylene-bis-acrylamide
MNPs	Magnetic Nanoparticles
Na-MMt	Sodium montmorillonite
SEM	Scanning Electron Microscope
%R	Percentage Removal
%GP	Percentage Grating Potential
%GE	Percentage Grafting Efficiency

CHAPTER 1

INTRODUCTION

1.1 Background of the study

The untreated wastewater is the major cause of environmental pollution which ultimately hinders the growth of a sustainability community. Rapid industrialization, uncontrolled urbanization, agricultural activities, and many other anthropogenic activities are responsible for wastewater production. Furthermore, improper disposal of waste into water bodies is also aggravating the situation. There are number of inorganic and organic toxins that are released into water resources from industries [1]. There are different types of organic pollutants present in water bodies such as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, greases, pharmaceuticals etc. Generally, organic pollutants have one or more cyclic ring either of aromatic or aliphatic nature, and a variable number of halogen substitutions. All these factors make them persistent in the environment. Inorganic pollutants includes metals and their compounds, such as the inorganic salts, mineral acids, oxides, trace metals, ores of metals, cyanides, and sulfates etc. They are very poisonous even at low concentrations and cause serious health problems [2].

Phenols and dyes are the pollutants of main concern now days due to their excessive use and toxicological impacts [3]. Phenol releases from industries and persists in environment for long periods of time. Phenol generally consists of aromatic 3 hydrocarbon ring and substituted hydroxyl group. These compounds are generally less soluble in water as compared to organic solvents. Phenols and its compounds are mostly used in the manufacture of resins, xylenols, cresols, alkylphenols. It is also released as a byproduct in the production of pharmaceutical products, dyes, indicators and germicidal paints etc [4].

Phenol is widely used in industrial sector, such as packaging, plastics, fabrics, and rubbers. The wastewater discharged from these industrial processes cause environmental and other hazards.

It is reported that concentrations of phenol ranging from 9–25 mgL^{-1} is harmful for humans and other organisms. Therefore, it is vital that techniques should be established for recovering and recycling of different phenolic compounds. Currently, phenolic compounds are removed from aqueous media using old methods such as coagulation, membrane separation, flocculation, extraction, and adsorption. Adsorption is the most preferred approach due to certain features such as pollution-free nature, high performance and cost-effectiveness [5].

Globally, the textile industries are responsible for approximately 75% of dyestuff marketplace and almost 10,000 varieties of dyes are applied for printing or coloring. This unnecessary usage of dyes contaminates the groundwater and surface water through effluent discharge. The living organisms in aquatic bodies suffer from low level of dissolved oxygen due to increased COD. Furthermore, they also affect the quantity of light penetrating into water, decreased the quantity of light penetrating into the water body, leading to more biochemical oxygen demand (BOD),and diminishing of activities of aquatic plants related to and thus negatively impacting the food source of aquatic organisms. Dyes are not harmful for environment but also for human health. Intake of water containing synthetic dyes can cause carcinogenic, genotoxic and mutagenic effects [6].

Crystal violet is a cationic dye and mostly utilized in paper, medical, and various other industries. It is known to be a most biohazardous substance as it is not only toxic or mutagenic but also genotoxic and carcinogenic in nature. Furthermore, CV has very dark color and has ability to cause disruption in aquatic environment. It is reported that even low concentration (e.g. 1 mg/L) of CV has potential to enhance the turbidity level of water and hence, hindering the photosynthesis process of aquatic plants. The exposure of CV to humans may cause respiratory

disease, chemical cystitis, eye irritation, kidney failure, permanent blindness, heart rate, and cancer [7].

1.2 Advanced Wastewater treatment technologies

Various wastewater treatment technologies are employed owing to the harmfulness of contaminants. The processes of wastewater treatment include advanced oxidation processes, attached growth treatment processes, membrane processes, ozonation, membrane bioreaction, coagulation, flocculation, etc. These above-mentioned methods are capable to treat specific types of particulates to some degree, but they are not capable enough to remove all other kinds of contaminants or pollutants that are present in wastewater [3].

1.2.1 Nanomaterials for wastewater treatment

There are different types of nanomaterials which are used for various applications [8]. The properties of nanomaterials such as nanoparticles or nanocomposites are different as compared to bulk materials. The integration of nanomaterials into the hydrogel has been of great interest due to various applications. The swelling abilities of hydrogel are attributed to the presence of hydrophilic functional groups (primary amidic, hydroxyl, carboxylic etc.) found in polymer matrices. The insoluble nature of hydrogel is due to crosslinking between the polymer chains. This crosslinking between chains is responsible for the three dimensional structure of hydrogel. The chemistry between hydrogel and other nanomaterials can be understood through crosslinking between network chains [9].This innovative incorporation of nanomaterials and hydrogel produces structural diversity. Mainly nanocomposite hydrogels are formed though covalent or physical bond between hydrogel and nanocomposite. Currently, different kinds of nanomaterials derived from metal (gold, silver), metal oxides (iron oxide, titanium oxide), inorganic compounds (silica, silicates), carbon nanotubes and graphene are combined with hydrogel to produce hydrogel nanocomposites with more enhanced functionalities, and mechanical strength [10].

1.2.2. Hydrogel Nanocomposites for wastewater treatment

Hydrogel nanocomposites have gained attention as potential materials for wastewater treatment due to their unique properties and capabilities. Moreover, these networks of hydrophilic polymers have the ability to absorb water or other fluids. When combined with nanocomposites, which are materials containing nanoparticles dispersed within a matrix, hydrogels can exhibit enhanced properties and functionalities for wastewater treatment [14].

Hydrogel nanocomposites can be engineered to have a high surface area and porous structure, enabling efficient adsorption of various contaminants from wastewater. Nanoparticles incorporated into the hydrogel matrix can enhance adsorption capabilities, thanks to their high surface area, surface reactivity, and specific affinity toward certain contaminants. Examples of nanoparticles used in hydrogel nanocomposites include activated carbon, graphene oxide, and metal oxide nanoparticles. Moreover, they can effectively remove heavy metals from wastewater through adsorption or ion exchange mechanisms. Metal-selective nanoparticles embedded in the hydrogel matrix can enhance the selectivity and efficiency of heavy metal removal. Additionally, functionalization of the hydrogel with ligands or chelating agents can improve the complexation of metal ions, enhancing their removal from the wastewater [14]. It's worth noting that the development and optimization of hydrogel nanocomposites for wastewater treatment is an active area of research. Factors such as the choice of polymers, nanoparticles, and fabrication methods can significantly impact the performance and efficiency of these materials.

Mucilage extracted from okra, also known as okra gum or okra polysaccharide, has been studied for its potential applications in wastewater treatment. Okra mucilage contains high amounts of polysaccharides, which give it its thick, gel-like consistency. These polysaccharides have shown promising properties for various environmental and industrial applications, including wastewater treatment. There are many potential uses of mucilage extracted from okra for wastewater treatment such as coagulation and flocculation. Okra mucilage can be

used as a natural coagulant and flocculent in wastewater treatment. When added to wastewater, it can help in the aggregation of suspended particles and colloids, making them easier to remove through sedimentation or filtration processes. Okra mucilage has shown comparable or even better coagulation and flocculation performance compared to traditional synthetic chemicals.

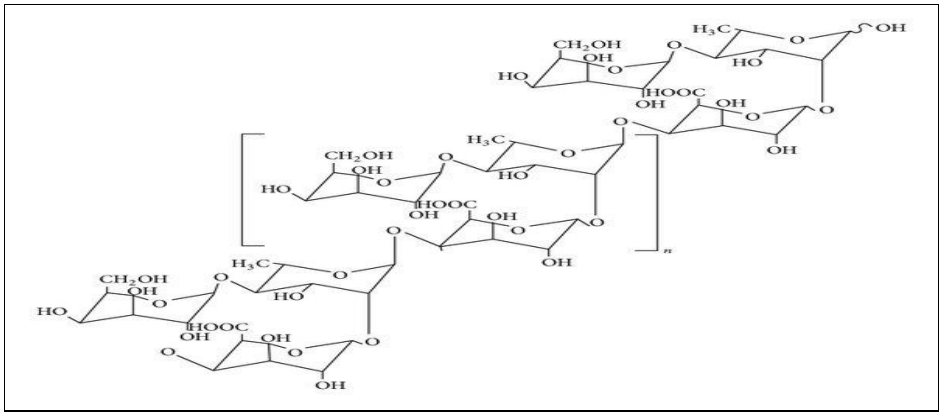


Figure 1.1. Polysaccharide of okra mucilage

The Okra mucilage has been investigated for removal of heavy metals from wastewater. The polysaccharides present in okra mucilage can form complexation bonds with metal ions, facilitating their removal from water. This process, known as chelation, can help lowering the heavy metals concentrations in wastewater, making it safer for discharge or reuse.

Moreover, okra mucilage has shown potential in adsorbing organic compounds present in wastewater. The polysaccharides can act as an adsorbent, attracting and binding to organic pollutants, such as dyes, oils, and organic solvents. This can help in reducing the organic load of wastewater and improving its quality. Additionally, one of the advantages of using okra mucilage in wastewater treatment is its biodegradability and environmental friendliness. Unlike synthetic chemicals, okra mucilage is derived from a natural source and has low toxicity. Its degradation by microorganisms minimizes the environmental consequences as compared to orthodox treatment methods [13].

The aim of present study is to utilize the waste material to produce valuable products. In present study sugarcane waste was used to extract biosilica. Biosilica has porous nature and large surface area, which makes it effective for removal of pollutants wastewater [11]. Biosilica was then incorporated in hydrogel synthesized from okra mucilage. The biosilica hydrogel nanocomposites were used for removal of phenol and crystal violet dye from wastewater.

RATIONALE

Industrial and municipal activities release a large quantity of polluted wastewater which is discharged to the surface water bodies without any proper treatment. In Pakistan, environmental quality is degrading day by day. Improper wastewater treatment and disposal is considered to be the responsible factor for deterioration of environmental quality as well as human health in Pakistan. Large amount of organic and inorganic pollutants increases the COD of wastewater that should be reduced before its discharge. Presence of phenol content even at low concentration increases the toxicity of wastewater. High level of phenols and dyes is not only injurious to the aquatic life but causes serious health issues to humans. Moreover, discharge of untreated wastewater containing toxic colored compounds is a threat for human beings and aquatic life. Persistence and toxic nature of dyes at even small amount of dye in environment may cause serious impacts. It is vital to develop economic and environment friendly techniques to remediate wastewater. The aim of this study was to synthesize biosilica hydrogel nanocomposite via greener approach and further apply them for the reduction of wastewater pollutants specifically phenol and removal of dye i.e. crystal violet from the water.

OBJECTIVES

The objectives of the study were:

- Synthesis of bioadsorbent i.e. biosilica hydrogel nanocomposites and their characterization (SEM & FTIR).
- Application of synthesized biosilica hydrogel nanocomposites for the removal of phenol and crystal violet dye from wastewater.

CHAPTER 2

LITERATURE REVIEW

With a rapid increase in industrialization, proper management and disposal of wastewaters is the biggest threat to the environment and it hinders the goal to achieve a sustainable development of the human society. Effluents discharged from different industrial sector such as paper, cosmetics, pharmaceuticals, textiles, and plastics is considered one of the most critical and serious problem [14, 15]. Treatment of wastewater to remove harmful pollutants and chemical substances is a critical issue.Many researches are carried out to investigate the behavior of hydrogels and nanomaterials for removing the dyes and phenolic compounds from wastewater. Few of them are mentioned below.

Sugarcane bagasse has high content for silica that's why it's a good approach to synthesize biosilica for wastewater treatment. Mohd *et al.* [16] carried out the synthesis of silica nanoparticles using sugarcane bagasse. The processes of precipitation and extraction were used due to certain reasons such as emission of less toxins, need of low energy, and economic feasibility. Furthermore, it was revealed that these Si NPs have amorphous nature with specific surface area of 111 m^2/g^{-1}, and average size of 30nm.

Similarly, Seroka *et al.* [17] carried out the green synthesis of biosilica from sugarcane bagasse. In this study, L- Tetrapropylammonium Hydroxide, and cysteine hydrochloride monohydrate acid were used for extraction of silica. This nanosilica was further examined using the analytical techniques to check chemical, structural and morphological properties. The results of SEM showed the silica nanoparticles were present in form of agglomerates having uneven shapes and sizes. It was also observed that few spherical particles were also present. The Si~O~Si bonds were observed at 461.231 cm^{-1}, 787.381 cm^{-1} and 1045.99 cm^{-1}. These all analysis confirms that silica was successfully extracted from sugarcane bagasse ash.

Alves *et al.* [18] used the agricultural waste for extracting biosilica. Various factors having potential to effect the particle production of silica were assessed carefully. The best state for production of biosilica was attained at temperature upto 80°C for 1 h. The synthesized silica possessed the amorphous nature with 99% purity. The results suggested that sugarcane waste ash can be used reducing the environmental impact.

The green adsorbents are particularly focused for reducing the water pollution. Prasad *et al.* [19] prepared biocomposite of biosilica for adsorption of chromium and copper ions from aqueous solution. The specific surface area and pore size were found to be 751.9 m^2/g and 7.21 nm. Additionally, various parameters such as adsorbent dose, initial concentration, contact time, and pH were studied in detail. The results revealed the adsorption capacities were 201.56 mg/g and 331.69 mg/g for Cr^{6+} and Cu^{2}+ ions, respectively.

The use of sugarcane bagasse for adsorption of Acid red 1 dye from wastewater was studied by Kamran *et al.* [20]. The synthesized biosorbent and biocomposite were characterized. The batch adsorption experiments were carried out and optimum conditions found at 2 pH , 0.05 g dose, 75 min contact time, 400 mg L^{-1} initial dye concentration, and 30 °C. The maximum adsorptive capacities were 143.4–205.1 mg g^{-1} due to binding sites and specific surface area.

Similarly, Lui *et al.* [21] reported a cross-linking method for the fabrication of silica hydrogel. The alkylsilane groups were grafted onto nanoporous silica. It showed great specific surface area of 51.3 $m^2g^{-1}$and good dye adsorption ability. Furthermore, colloidal electrokinetic potential analysis also exhibited the exceptional adsorptive capacity of cationic dyes. The hydrophobic interactions studies revealed the adjustment of dye adsorption phenomenon by changing various concentrations reagents found in hydrogel. This clearly demonstrates the practical usage of this synthesized silica hydrogel. The adsorption efficiency was found up to 90% by regenerating the gel for almost 6 cycles.

Similarly, El *et al.* [22] carried out alkaline treatment followed by a bleaching process to produce biodegradable cellulose from sugarcane bagasse. It was used for removal of two dyes i.e. Crystal violet and Methylene blue. The functional groups of treated sugarcane bagasse were examined using analytical techniques. The variables such as dose, contact time, initial concentration, and NaCl dose were also studied. For the CV and MB-dyes, the maximum adsorption capacities were (q_{max}) 107.5 and 112.9 mg/g, respectively. The adsorbent was discovered to be an efficient, cost-efficient, and eco-friendly.

Sujan *et al.* [23] introduced the bi-functional silica crosslinker for immediate augmentation of swelling capacity of hydrogels. The swelling capacity and mechanical properties were two important features of the hydrogels. These bi-functional silica nanoparticles have amine groups that have potential to offer the pseudo-crosslinking effects. The polyacrylic acid (PAc-Si) and polyacrylamide (PAm-Si) hydrogels were prepared. The hydrogels were incorporated with BF-Si crosslinkers and exhibited prominent improvement in mechanical properties and swelling capacity. The swelling ratio for PAc-Si was 60 and for PAc-MBA was 40 .This smart strategy can also be used for fabrication of many other hydrogels such as vinyl or acrylate polymer hydrogels.

Tamer *et al.* [24] synthesized the graphene oxide (GO) comprising sodium hydroxyethyl cellulose (HEC) hydrogel beads and alginate (SA) for CV adsorption. The high adsorption capacity toward CV molecules was observed i.e. 123.16 mg g^{-1} to 312.72 mg g^{-1} at pH 5. The Temkin and Langmuir isotherms were used to determine the monolayer adsorption of CV. The results showed that adsorption process was spontaneous and 79.4% removal of CV was achieved.

The adsorption of dyes using hydrogels has played an important eco-friendly role. Silva *et al.* [25] synthesized the hydrogels using the conventional method (CM) and microwave-assisted method (MWM) for adsorption of azo dye Acid Blue 113. The MW and CM hydrogels followed the Freundlich and Langmuir and

isotherm models, respectively. The microwave assisted hydrogel proved to more effective for removal of dye molecules for wastewater.

Another study by Lv *et al.* [26] utilized sodium alginate and *S. fusiforme* polysaccharide (SFP/SA) to make a hydrogel. The study revealed that as SFP content grew, its cohesiveness increased, and thermal stability improved. The adsorbents effectively removed the CV molecules effectively. There were other significant factors than the intraparticle diffusion of CV dye. SFP/SA has shown a strong potential for regenerative adsorption. At the tenth successive cycle, its adsorption rate remained at > 97%, whereas SFP accounted for 80%.

Moreover, Wu *et al.* [27] prepared semi-IPN hydrogels through a chemical cross-linking process. Various analytical techniques and rheological measurements were used to investigate the chemical and physical features of semi-IPN hydrogels. Moreover, these hydrogels demonstrated the good adsorption (107 mg/g) towards crystal violet. The entire adsorption process was explained with help of Langmuir isotherm model. This study proves that semi-IPN hydrogels are very promising for CV adsorption.

In another study, Santos *et al.* [28] carried out the preparation and characterization of poly composite hydrogel. The adsorbent was synthesized from poly-melamine-formaldehyde and sodium silicate. The precursor for silica nanoparticles (Si-NPs) was sodium silicate. Further, adsorption potential of MB in hydrogel, rehydration, potential of zero charge (PZC), and dehydration were also evaluated. The results indicated excellent adsorption of MB (q_{max} of 140 mg/g) by this poly composite hydrogel.

Dyes are very toxic even at low concentrations and their exposure is very harmful not only for humans but also for aquatic bodies. Therefore, many scientific experiments have been performed to treat wastewater containing dyes. Basaleh *et al.* [29] conducted experiment using industrial waste and for this purpose acrylamide-acrylic acid copolymer (AA) was introduced to baghouse dust (BHD) to get AABHD composite. This composite was then used for removing cadmium,

lead, and methylene blue. The different analytical techniques were used to characterize the adsorbent. Various parameters were analyzed for the evaluation of adsorption performance of AABHD hydrogel. The results indicated that adsorption efficiencies were 96%, 98%, and 98% and capacities were 503, 236, and 476 mg/g for MB, Cd and Pb respectively. Hence, it can be inferred that wastewater can be treated with AABHD as it is efficient for adsorption of MB and metal ions.

The toxic dyes are very difficult to eliminate and hence, destructive for the humans and environment. So, it's high time to make use of eco-friendly practices for removal of dyes. Aljar *et al.* [30] studied the adsorption of methylene blue using nanocomposites hydrogel beads system. The adsorbent removed dye up to 90% after six consecutive adsorption-desorption cycles. The Langmuir isotherm was applicable and maximum adsorption capacity was 51.34 mg/g.

Radhy *et al.* [31] synthesized composite hydrogel using polymerization of maleic acid and acrylic acid to remove the CV. The Langmuir isotherm models were shown to provide a good description of adsorption, and the synthesized adsorbents demonstrated high removal efficiency for crystal violet.

For the removal of phenol, Wang *et al.* [32] conducted an experiment. The composite hydrogels based on graphene oxide (GO) and hydroxypropyl cellulose (HPC) was produced. The single network composite hydrogel (SNCH), and the double network composite hydrogel (DNCH) were produced. The DNCH has a higher adsorption capability and more functional groups. The adsorption capacities of DNCH and SNCH were 213.5 and 136.5 mg/g respectively, at pH 7 within 120 minutes. After six adsorption-desorption cycles, the SNCH and DNCH were utilized without experiencing reduction in the initial binding affinity. This demonstrated that composite hydrogels are suitable in practical applications.

Currently, hydrogel nanocomposites are produced using different kinds of nanomaterials such as nanocomposites or metal nanoparticles metal oxides, inorganic, and graphene incorporated into hydrogels [10]. Wang *et al.* [33]

prepared grapheme nanocomposite hydrogel for adsorption of phenol. These nanocomposite hydrogel showed excellent mechanical characteristics and removed 74% of the initial 4-NP. The adsorbent proved to be a good alternative for removal of phenolic compounds from aqueous solutions.

In another study, Nakhjiri *et al.* [34] synthesized magnetic double-network nanocomposite hydrogel by using copolymerization method. The adsorbent was characterized and its adsorption performance was checked for 4-nitrophenol and phenol. The results exhibited that phenol and 4-nitrophenol were removed up to 77% and 83% at pH 7, respectively. Hence, this hydrogel proves to be appropriate adsorbent for the removal of these phenol and 4-nitrophenol.

Iron can be used to synthesize low cost adsorbents. Iron nanoparticles coated with hydrogels are widely used for treatment of wastewater treatment. Shen *et al.* [35] conducted coprecipitation process to prepare the Fe_3O_4 magnetic nanoparticles with hydrogel coating (Fe_3O_4@hydrogel). It was exhibited that Fe_3O_4 surface was perfectly coated with hydrogel. This hydrogel coated Fe_3O_4 was employed as a catalyst for degradation of phenol in a Fenton-like reaction. The results from experiment have shown that approximately COD and phenol were removed up to 80.4% and 98.2% respectively.

Many studies are carried out that shows efficient removal of pollutants through crosslinking between nanoparticles and hydrogels. Rahman *et al.* [36] carried out a study for synthesis of hydrogels based on crosslinking between reactive copolymers and silica nanoparticles. The synthesized silica nanoparticles cross-linked acrylamide hybrid hydrogels were used for treatment of MB. Different types of polymers such as *p*MS and *p*AS were used during this process. Various important factors i.e. temperature, initial concentration, adsorbent dose, pH, and contact time were also analyzed. The results indicated that Langmuir model was better fitted and maximum adsorption capacities were 588.23 and 666.65 mg g^{-1}, for *p*MS-Si and *p*AS-Si respectively. Furthermore, the synthesized adsorbents showed high selectivity towards MB dye molecules.

A study by Mittal *et al.* [37] prepared the hydrogel nanocomposites using xanthan gum (XG-HNC) for removal of CV molecules. The maximal adsorption capacity was found to be 1566.97 mg/g, and followed a pseudo-second-order rate equation. Moreover, the adsorption behavior of these hydrogel nanocomposites was also verified, to check out its potential for treating the dye molecules. Additionally, the reusability of XG-HNC was evaluated over the course of 20 continuous adsorption-desorption cycles. As a result, XG-HNC is a strong option for the adsorption of cationic dyes from wastewater due to its distinct structure and characteristics.

Use of hybrid treatment method combining hydrodynamic cavitation (HC) for removal of CV dye molecules from aqueous medium was examined by Raj *et al.* [38]. Using the ultrasound polymerization method, a poly-acrylamide (PAM) nano-composite hydrogel with embedded TiO_2 nanoparticles was generated. Hydrodynamic cavitation was used to degrade the CV dye, and a hydrogel adsorption column was used to subsequently adsorb the dye molecules. In comparison to its individual operation, the hybrid system accelerates the removal of dye at hydrogel loading of 5 g/L and inlet pressure to orifice at 3 bar. To determine the adsorption behavior, Langmuir and Freundlich isotherm models were assessed.

Hydrogels made of a starch-graft-poly(acrylic acid) (SPAA) starch-grafted magnetic Fe_3O_4@SiO_2 nanocomposite were produced by Pourjavadi *et al.* [39] and employed as absorbents for effective adsorption of CV from aqueous solutions. Due to the high magnetic sensitivity of the nanocomposite hydrogels, they could be magnetically separated from water without causing secondary contamination. The results showed dye removal upto 85% with a small amount of magnetic SPAA nanocomposites. According to the findings, addition of polysaccharides can boost the hydrogel microsphere's cohesion, and its ability to better bind crystal violet dye.

In another study, Basaleh *et al.* [40] investigated adsorption of two dye i.e. methyl orange (MO) and methylene blue (MB) using an efficient magnetic adsorbent that is Poly (acrylamide acrylic acid) grafted on steel slag. During this study, polymeric composite was prepared from steel making waste. This process carried out modification of steel slag with acrylamide acrylic acid resulting in formation of (SSAA) copolymer. This polymer was used for removal of MB and MO from synthetic solution.

Physical adsorption and chemisorption mechanisms on polymer were observed for MB and MO. The MB and MO have maximum adsorptive capacity of 463 mg/g and 47 mg/g. The maximum removal efficiencies of 94% and 97% were reported for MB and MO respectively. This process was feasible enough to be used effectively for elimination of cationic and anionic dyes from wastewater.

Singh *et al.* [41] carried the adsorption of malachite green dye by semi-interpenetrating network synthesized using Psyllium-Okra hybrid backbone. The crosslinkers and initiators were also used such as ammonium persulphate and acrylamide. The adsorbent removed up to 62.38% dye at optimum conditions such as 1 g dose, initial concentration 10 mg/l and time interval of five minutes. Thus, results indicated that semi-IPN was very efficient for removal of heavy metal ions and dyes.

Furthermore, Ahmad *et al.* [42] investigated removal of crystal violet using peels of kiwi fruit and synthesized an adsorbent named polyacrylamide-grafted *Actinidia deliciosa* peels powder (PGADP). Different batch experiments were performed with varying pH, temperatures, contact time, initial concentrations, and adsorbent doses. The result showed that crystal violet dye was efficiently removed at contact time of 180 minutes, initial dye concentration of 20 mgL^{-1}, and pH 7.3. Hence, PGADP can effectively remove CV dye from aqueous solution and industrial wastewater.

CV dye is a toxic organic dye that is responsible for many health complications and environment pollution. Cheruiyot *et al.* [43] investigated the use of Waste

Coffee Husks (WCH) for removal of CV dye. Various factors such as dye concentration, adsorbent dose, pH, and contact time were evaluated. Moreover, the result showed that adsorption was highly favorable in at low temperatures. As surface area, contract time and initial concentration were increased, the rate of dye adsorption also increased. The CV was removed up to 94% at pH 3 and 10 mins. The results showed that this Coffee Husk is very economical and cost effective.

Kumar *et al.* [44] studied the adsorption of CV from the aqueous solution onto treated ginger waste .The parameters included the pH, initial dye concentration, contact time, and temperature. The kinetic data were evaluated using the pseudo-first order, and pseudo-second order models. The maximum monolayer biosorption capacity was found to be 64.93, 227.27 and 277.7 mg/g at 30, 40 and 50 °C, respectively.

One of the main ecological issues faced by the world right now is synthetic dye waste. Algal biomass has become a potentially effective substitute for the treating wastewater. Essekri *et al.* [45] focused on the functionalization of brown algae (BA) by citric acid to improve its ability to adsorb dyes from textiles in aqueous solutions. The novel functionalized brown algae's morphological texture and surface chemistry were studied. Investigations were made into BA-CA's effectiveness at removing the crystal violet (CV) dye from wastewater. The thermodynamic characteristics strongly demonstrated the physiosorption, and spontaneous behavior of the CV elimination process. The regeneration investigation revealed that the BA-CA may be reused up to five cycles with outstanding results.

The effectiveness of ex-situ crosslinked gellan gum/bacterial cellulose hydrogels as effective absorbents for the removal of safranin and crystal violet dye pollutants was examined by Nguyen *et al.* [46]. Citric acid (CA), a green crosslinker, was used in preparation as it is low-cost, and simple crosslinking technique. The analytical techniques were used for physicochemical and mechanical features of crosslinked hydrogels. Investigation into the hydrogels'

ability to remove dye revealed that, adsorption rate was higher for safranin dye, then crystal violet, with maximam adsorption capacities of 17.57 and 13.49 mg/g, respectively. Moreover, the results indicated that it was exothermic process as shown by the temperature dependency analysis.

For the elimination of total phenolics and photocatalytic discoloration of high strength olive mill wastewater (OMW), the solid olive wastes-based adsorbent (CuOOC) with photocatalytic power was developed by Yuney *et al.* [47]. The results of the Brunauer-Emmett-Teller and FTIR investigations clearly demonstrated that CuO-OC oxygen-containing functional groups most likely took part in the adsorption of total phenols from the OMW via electrostatic, hydrogen-bonding, and interactions. Additionally, after adsorption, the overall pore volume of CuOOC reduced from 0.068 to 0.052 cm^3 g^{-1}, indicating that phenolics were likely trapped in the micro- and mesopores of CuOOC. According to the adsorption kinetics, 82.7-95% of the phenolic compounds were removed in the first 360 minutes that is more quick removal rate compared to other adsorbents and techniques. The reuse efficiency of CuOOC remained at 60% after 5 consecutive recycling.

CHAPTER 3

METHODOLOGY

3.1. Chemical and Materials

Sugarcane bagasse ash, Phenol, Crystal Violet (CV), ammonium persulfate (APS), acrylamide (AM), N, N'-methylene-bis-acrylamide (MBA), hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid (CH_3COOH), distilled water, Sodium carbonate (Na2CO3) sodium nitrate (NaNO3), 4-nitroaniline (C6H6N2O2).

3.2. Collection of material

Okra plant (*Abelmoschus esculentus*) and sugarcane bagasse were collected from the local market and vendors.

3.2.1. Preparation and Acid Treatment of Sugarcane Bagasse Ash

After the collection of sugarcane bagasse, it was sun-dried and completely burned using a furnace to get more fine particles of ash. This ash was stored in an airtight plastic container.

The synthesis of Biosilica started with the acid treatment of ash. For this purpose, 50g of ash was dissolved into 250 mL water, and 0.1 M HCl was added to it. It was put on an orbital shaker for 2-4 hours. Then this solution was filtered and oven dried for overnight at 120 °C temperature. The dried acid treated ash was grinded with mortar and pestle. This ash was stored in a plastic box. Figure 3.1 shows the dry sugarcane bagasse and acid treatment process.

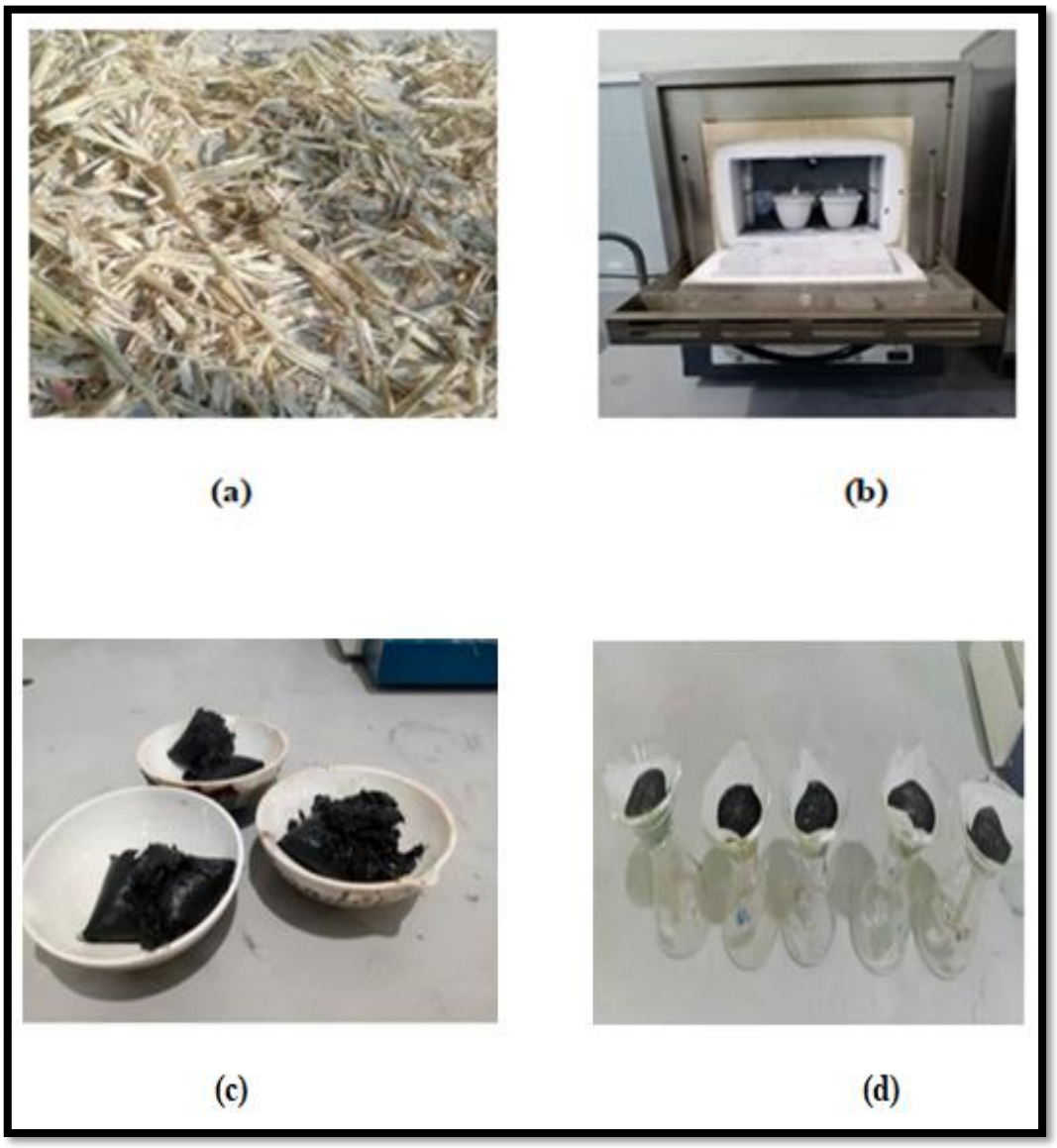


Figure 3.1 (a) Dry Sugarcane Bagasse (b) Ash containing crucibles in furnace (c) & (d) Acid Treatment

3.2.2. Preparation of Okra Powder

Okra was collected from the local market and washed to remove any dirt residue. The seeds from the okra pod were removed as they do not hold the mucilage. These pods were down and sundried. After sundry, the electrical grinder was used to grind the pods to make a fine powder. This powder was oven dried to prevent any kind of humidity and fungus formation and further kept in a plastic container.

3.3. Synthesis of Mucilage, Biosilica, and Biosilica Hydrogel Nanocomposites

3.3.1. Mucilage Extraction from Okra Powder

The mucilage was extracted from okra pod powder through a sequential process as explained by Mohammadi et al. [48]. The distilled water was added in pod powder with the ratio of 30:1 water to okra powder for extraction of mucilage and stirred gradually by using a magnetic stirrer for 6-7 hours. This solution was filtered properly with a white muslin cloth. After that, the acetone was added 3 times to the quantity of filtrate while stirring. This reaction mixture was washed with ethanol for the removal of impurities. Lastly, the collected mucilage was oven dried at 100 ℃ for 2-3 hours. The final product obtained was ground with the help of mortar and pestle.

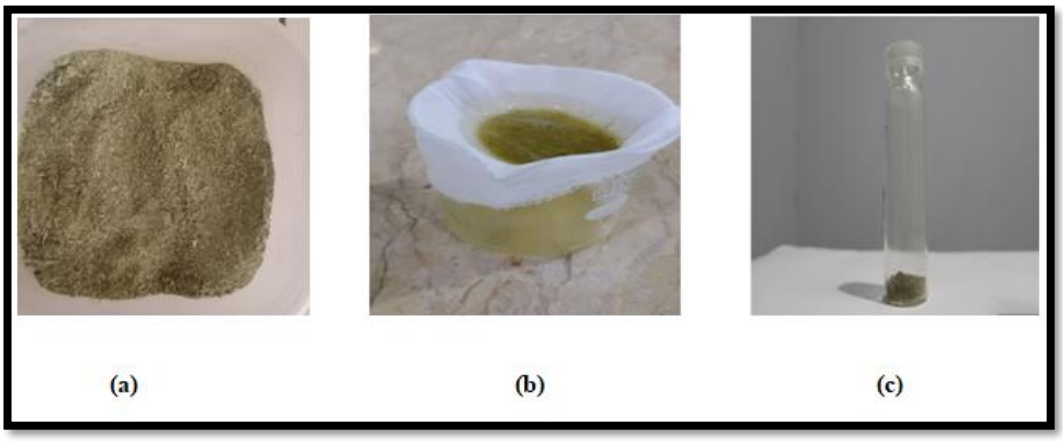


Figure 3.2 (a) okra powder (b) filtration with muslin cloth (c) Mucilage

3.3.2. Synthesis of Biosilica

For preparing the silica, NaOH and distilled water were mixed in a 500ml flask and then ash was added to it. The mixture was placed on a hot plate at 100°C for 2 hours stirring. The solution was cool down and filtered. The residue (ash) on the filter paper was washed with hot water. Then acetic acid was added to the solution drop wise to adjust the pH to 7. After adjusting the pH, the flask was covered with aluminum foil. After one day, the gel formed in the flask was washed with distilled water and then filtered. The filtrate silica was dried in an oven for 24hrs at 80°C. The dry form of biosilica was crushed into fine particles.

Figure 3.3. (a) Acid treated ash for silica extraction on hot plate (b) Solution pH adjusted to 7 by adding acetic acid (c) Silica gel (d) Silica gel sol. filtration (e)Silica gel after drying (f) silica powder placed in vial

3.3.3 Synthesis of Hydrogel

The hydrogel was prepared through using the graft copolymer process as described by Mittal et al. [42] with the slight alterations. The different compositions of hydrogels were synthesized using the initiator, monomer and cross linker (Table 3.1). These different hydrogels were oven dried at 70^{o}C for 2hr and then grinded to obtain powder.

Table.3.1. Feeding Composition and Preparation Conditions of Hydrogel

Sample no.1	Mucilage (g)	APS (initiator) (g)	AM (monomer) (g)	MBA (crosslinker) (g)	Total Yield(g)	Dry Polymer(g)	Irradiation Time
1	2	0.1	2.5	0.1	2.7	2.8	40
2	2	0.1	2.5	0.2	2.8	2.84	40
3	2	0.1	2.5	0.4	3	3.03	40

3.3.4. Swelling Studies of Hydrogel

To find out the swelling of hydrogel, a constant amount of hydrogel was added into distilled water and checked after every hour by weighing it. The equation used to determine the percentage swelling of samples is given below

Percentage Swelling (%) = W_s-W_o/W_o x100……. (1)

Where,

W_s = Weight after swelling

W_o = Weight before swelling

3.4.2. Estimation of Grafting Parameters

In order to find the most appropriate grafter hydrogel among all the samples, the percentage grafting and grafting efficiency experiments were conducted. For the percentage grafting. The hydrogel was weighted before and after the oven drying process for evaluation of percentage grafting. Following equations were used.

Percentage Grafting (%) = W_g-W_o/W_o x100…… (2)

Where,

Wg = Grafted Weight

Wo = Ungrafted Weight

Percentage Grafting Efficiency (%) = W_2-W_1/W_3 x100……. (3)

Where,

W_1 = Monomer weight

W_2 = Dry Polymer weight

W_3= Okra mucilage weight

3.3.5. Synthesis of Biosilica Hydrogel Nanocomposites

The polymeric hydrogel-based Biosilica will be synthesized from the procedure described by Fahdil et al. [49]. The 1g of okra mucilage powder was dissolved in 10 mL of distilled water. For the synthesis of hydrogel, different amounts of ammonium persulfate (APS), acrylamide (AM), N, and N'-methylene-bis-acrylamide (MBA) were taken i.e. 0.05g, 1.25g, and 0.2g respectively, and added into the beaker containing the mucilage powder. In a separate beaker, 0.2g of silica was dissolved in 20 mL of deionized water and was sonicated for good dispersion. Later, the sonicated silica suspension was added to the other reaction mixture. The whole reaction mixture was stirred well with the help of magnetic stirring and oven dried for 3 hours at 100 ℃.

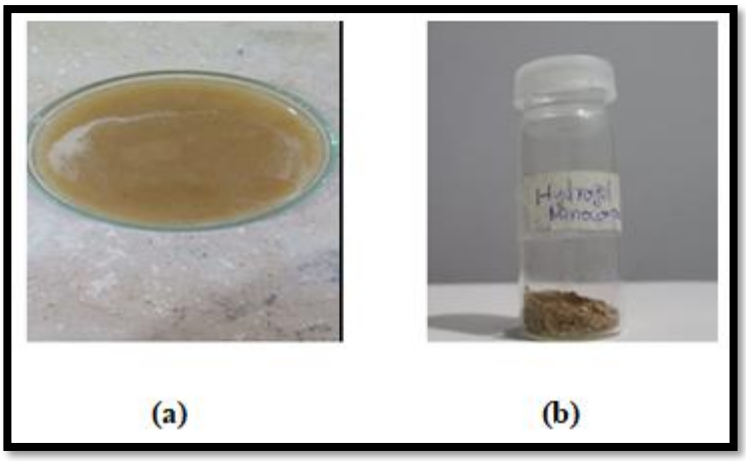


Figure 3.4. (a) Silica Hydrogel Nanocomposites after filtration (b) Silica Hydrogel Nanocomposites in powder form

3.4. Characterization of Biosilica Hydrogel Nanocomposites

The prepared Biosilica Hydrogel Nanocomposites are characterized by using the following techniques;

- Scan electron microscope (SEM) was used for the identification of morphology
- Fourier-transform infrared spectroscopy (FTIR) was used for the identification of the functional groups.

3.5. Adsorption experiments for phenol and crystal violet removal

Phenol was analyzed using the photometric analysis using the 4-Nitroaniline solution, sodium carbonate solution and sodium nitrate solution and crystal violet through UV-Visible spectroscopy. Moreover, various batch experiments were conducted for the adsorption of phenol and crystal violet from aqueous solution prepared in lab. These batch experiments efficiently analyzed the potential of nanocomposites for treatment of crystal violet and phenol. While carrying out these experiments several parameters were taken in to account i.e. pH, initial concentration, doses, and time.

3.5.1. Standard preparations for phenol and crystal violet

Following concentration of phenol solutions such as 0.25 ppm, 0.5ppm, 1.0ppm, 2.5ppm, 3.5ppm, 5ppm, 6ppm, 8ppm, 10ppm were prepared using the stock solution of phenol. In a conical flask 20 ml of each standard solution was taken and 2ml of 4-nitroaniline solution and 0.5ml of sodium nitrate solution were added. These solutions were measured through UV-Visible spectroscopy at 470nm after 10 minutes. The standard curve graph was plotted by taking the concentration values on X-axis and absorbance values on Y-axis. A straight line was plotted on graph and R^2 value was calculated. Afterwards, equation of linearity was employed to find out the unknown concentration of sample.

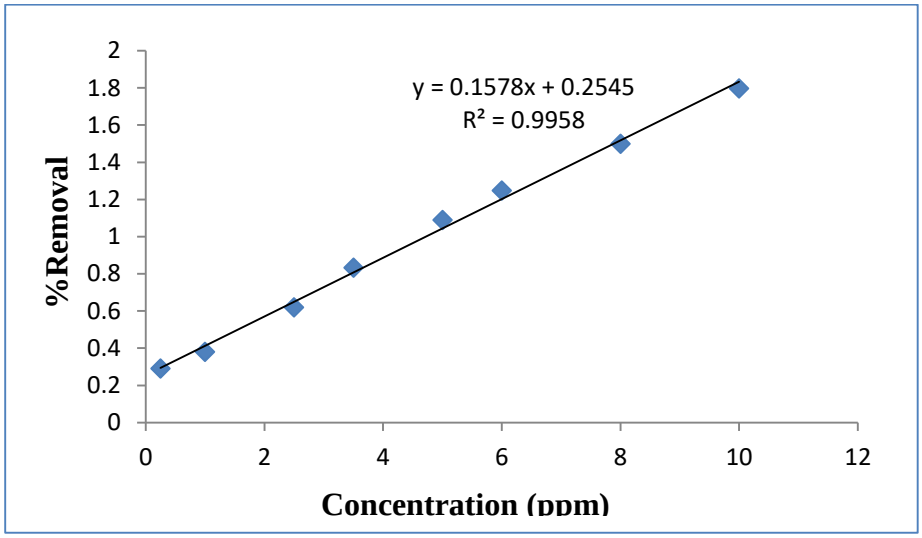


Figure 3.5.Phenol Standard Calibration Curve

In case of CV, five dilutions ranging from 1-30ppm (1ppm, 5ppm, 10ppm, 20ppm, 30ppm) were prepared using stock solution of crystal violet. These solutions were measured through UV-spectrophotometer at 590nm.

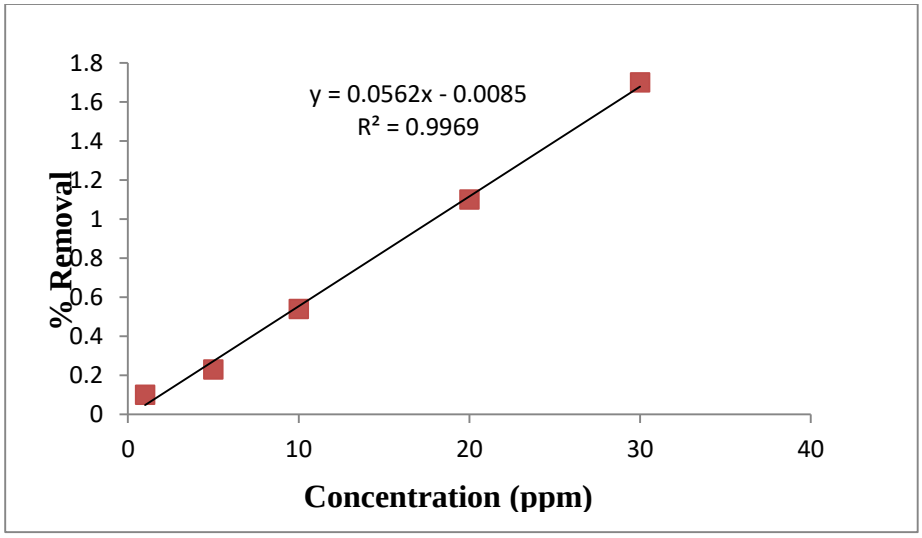


Figure 3.6.Crystal Violet Standard Calibration Curve

3.5.2. Effect of Adsorbent Doses

Various adsorbent doses were selected for adsorption of phenol and CV. For phenol, the dose range from 0.05g-0.4g was taken in 200ml solution while initial concentration was kept 10ppm and shaking time was 15 minutes on orbital shaker. For crystal violet, the dose range was 0.025g-0.5g was taken in 250ml solution while the while initial concentration was kept 25ppm and shaking time was 30

minutes on orbital shaker. After the desired contact time, filter paper was used to filter the solutions.

3.5.3. Effect of Initial concentration

To determine the effect of initial concentrations of phenol following concentrations were selected: 0.5ppm, 2.5ppm, 5ppm, and 10ppm. The others factors were kept constant such as 0.4g dose and shaking time of 15 minutes. Similarly, a range of initial concentration chosen for crystal violet was 5ppm, 10ppm, 20ppm, and 30 ppm and other factors were 0.1g dose and 30 minutes shaking time.

3.5.4. Effect of pH

To investigate the effect of pH on phenol and crystal violet removal, the pH were adjusted o by adding 0.1 HCl and 0.1 NaOH. The pH range was kept 2-12 for phenol. The others factors were kept constant such as 0.4g dose, 10ppm, and shaking time of 15 minutes. Likewise, a range of pH chosen for crystal violet was 2-12 and other factors were 0.1g dose, 25ppm, and 30 minutes shaking time.

By using equation 4, percentage removal was calculated for phenol and crystal violet. Equation 5 is the adsorption capacity (Qe) of phenol/CV removal i.e., adsorption capacity is the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent, was calculated.

$$\% \text{ removal} = \frac{(C_\circ - Ce)}{C_\circ} \times 100 \ldots. (4)$$

$$Qe = \frac{(C_\circ - Ce) * V}{m} \ldots. (5)$$

Where, Qe is the amount of phenol removed at equilibrium (mg/g), Ci is the initial concentration of phenol/CV in solution (mg/L), Ce is the final phenol/CV concentration in solution (mg/L), V is the volume of phenol/CV solution (L) and m is the mass of adsorbent (g).

3.5.5. Effect of Contact Time

The rate of phenol and crystal violet adsorption by silica hydrogel nanocomposites was also studied at different time intervals. The three different time intervals were selected i.e. 15- 60 minutes while keeping the other factors were constant such as the adsorbent dose at 0.4g, initial concentration 10ppm and pH 7. The values for absorbance were checked before adding reagents or after adding reagents. In the same way, different time intervals were also selected for CV removal i.e. 15-120 mins while other factors were 0.4g dose, 25ppm, and pH 12.

3.6. Adsorption Isotherms

The correlation between the amount of phenol/CV adsorbed qe(mg/g) and their concentration is presented by adsorption isotherms. The interaction between sorbent and the adsorbate molecules to reach equilibrium is well depicted by these adsorption isotherms. The experimental data was evaluated with the help of Langmuir and Freundlich isotherm models.

The Langmuir isotherm demonstrates that adsorbate shows maximum adsorption at homogenous saturated monolayer sites. The equation used to explain the Langmuir adsorption isotherm is given below.

$$\mathbf{C_e/q_e = 1/ q_m K_L + C_e/q_m \ldots\ldots\ldots (6)}$$

qe= mg of adsorbate per g of adsorbent at equilibrium (equilibrium uptake)

qm=mg of solute adsorbed per g of adsorbent

K_L=Langmuir constant (liter of adsorbent per mg of adsorbate L/mg)

Ce= equilibrium concentration of adsorbate in solution (mg/L)

The Freundlich isotherm model explains that when adsorbed molecules interact with each other, the adsorption occurs on heterogeneous surfaces.

$$\mathbf{\log q_e = \log K_f + 1/n \log C \ldots\ldots\ldots\ldots (7)}$$

Where

qe = mg of adsorbate per g of adsorbent at equilibrium (mg/g)

K=Freundlich constant that is an approximate indicator of adsorption capacity

1/n=Heterogeneity factor which is related to adsorption intensity

Ce = concentration of adsorbate in solution (mg/L)

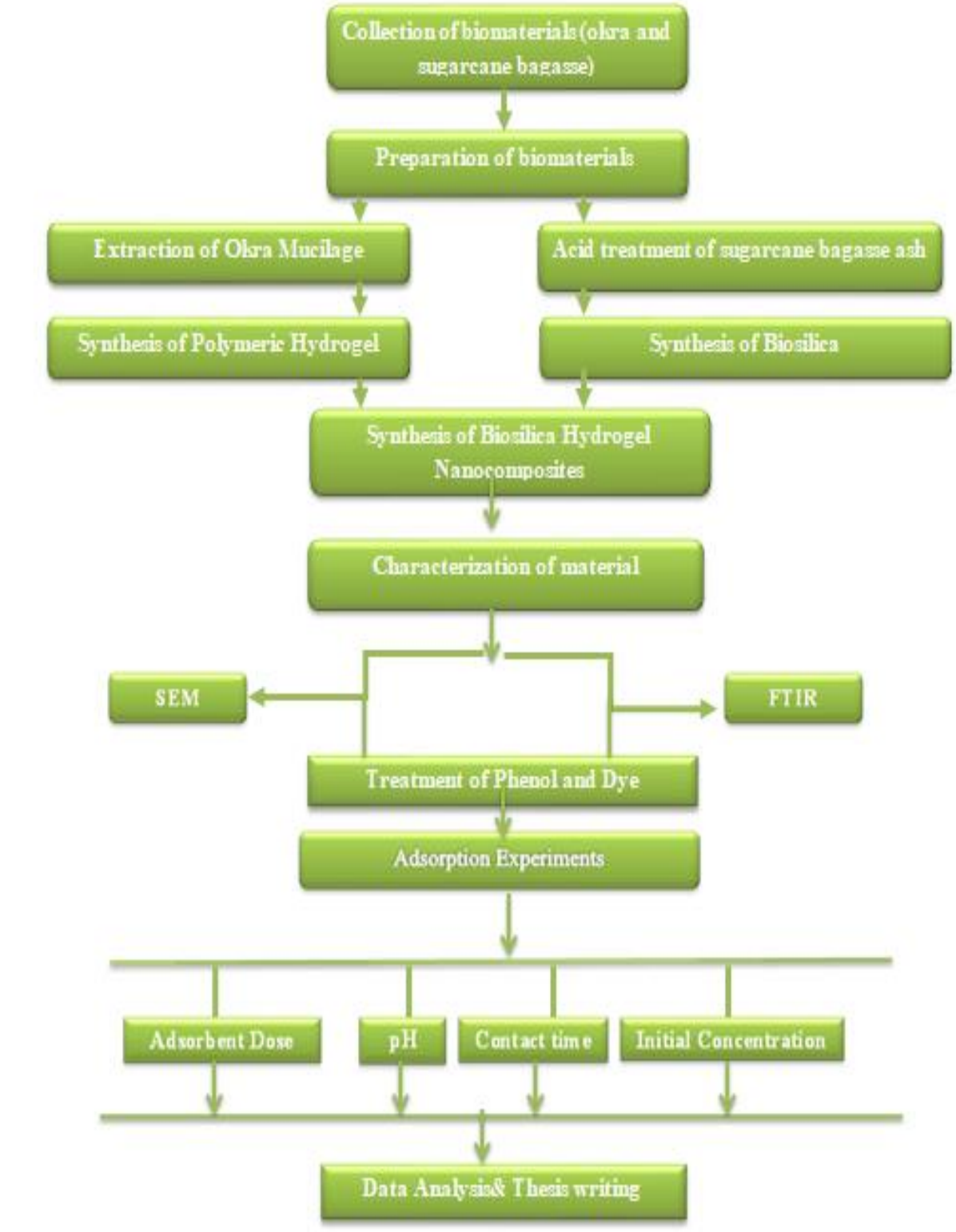


Figure.3.7. Flow sheet of methodology

CHAPTER 4

RESULTS

In the present study, Silica Hydrogel Nanocomposites were prepared by using sugarcane bagasse waste and okra pods. The adsorbent was further utilized for adsorption of removal of phenol and crystal violet dye from the aqueous solution. Various batch experiments were performed to study the effect of parameters i.e. time, adsorbent dose, pH, and initial concentration for removal of phenol and crystal violet dye from wastewater.

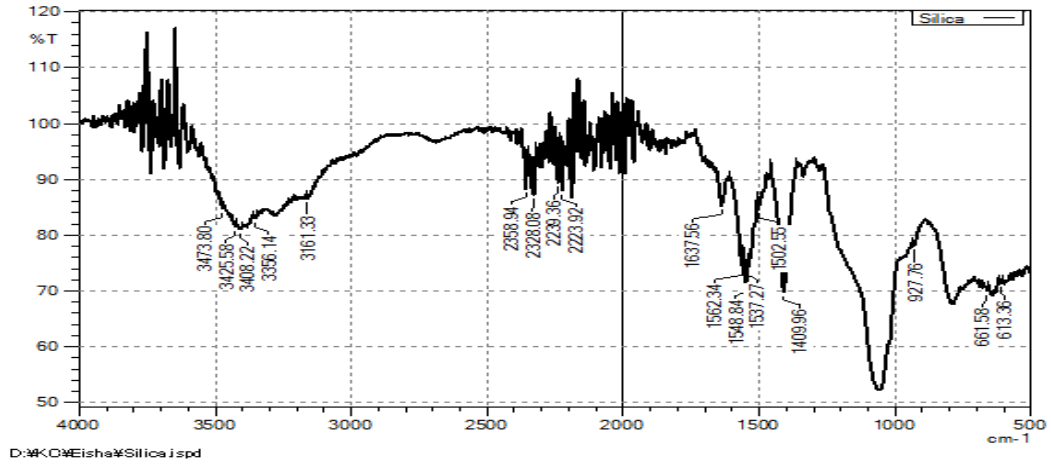
4.1. Characterization of synthesized adsorbents

4.1.1. Fourier Transform Infrared (FTIR) analysis results

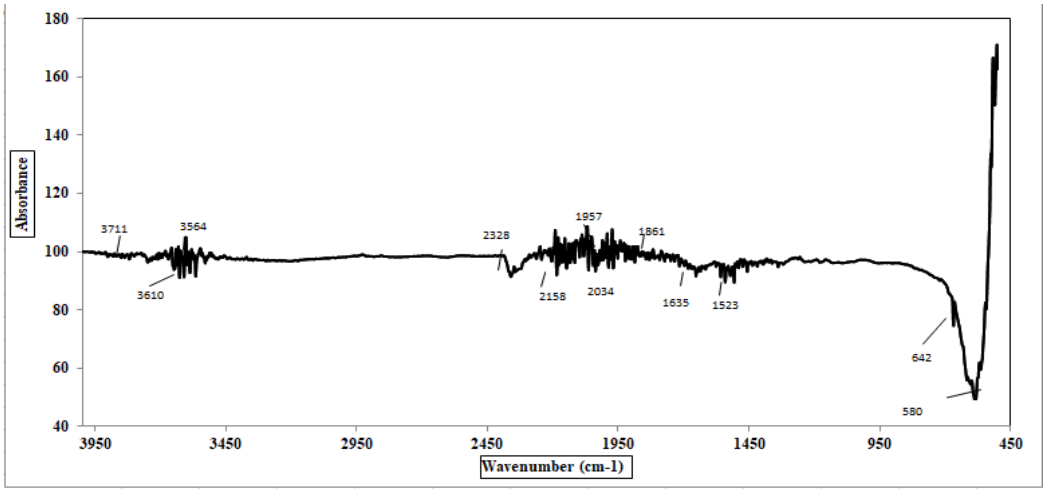
The biosilica hydrogel nanocomposites were analyzed through the FTIR to determine the functional groups present in prepared material. The FTIR spectrum of biosilica is shown in Figure 4.1(a). The spectrum band at 3522.15 to 3356 cm^{-1} and 3161.33 cm^{-1} shows N-H stretching and shows the presence of secondary amine. The stretching at 2358.94, 2328.08, 2239.36, 22223.92 cm^{-1}, shows the presence of strong O=C=O bond representing the carbon dioxide group. 1637.56 cm^{-1} shows strong C=C stretching (alkene group), while the stretching at 1562.34 , 1548.84 , 1537.27, 1502.25 cm^{-1} is due to N-O bond, and 1409.96 cm^{-1}shows the presence of sulfonyl chloride due to S=O cm^{-1} stretching. The 661.58, 613 cm^{-1} is due to presence of halo compound and C-I stretching [50].

The FTIR spectrum of synthesized hydrogel is shown in Figure.4.1 (b). The bonding at 3711, 3610 and 3564 cm $^{-1}$ is due to alcoholic groups. The presence of O=C=O bond is indicated at 2328 cm $^{-1}$. The bands observed at 2158 and 2034 cm $^{-1}$ is due the stretching of N=N=N group. The N=C=S group marks its presence at 2034 and 1957 cm $^{-1}$. The presence of anhydride group C=O bond and anhydride group is well exhibited at 1861 cm $^{-1.}$ The stretching at 1635cm $^{-1}$ shows the presence of alkene group along with the C=C band. The band at 1523 cm $^{-1}$ shows N-O bond [51].

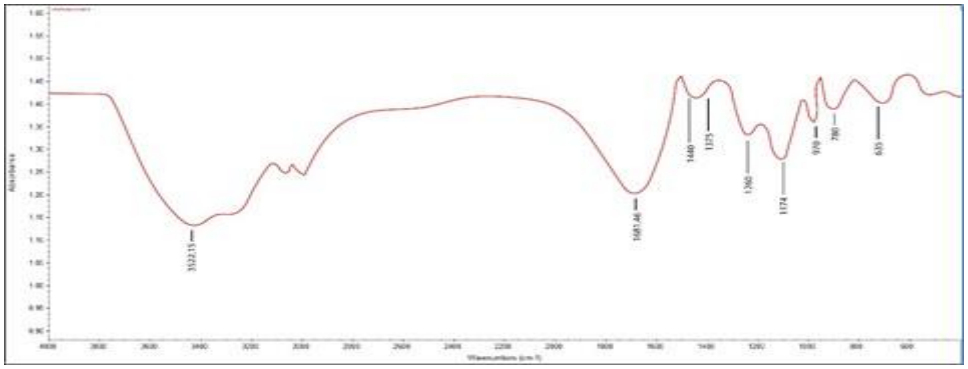
The FTIR spectrum of biosilica hydrogel nanocomposites is shown in Figure 4.1(c). The spectrum band at 3522.15 due to the N-H stretching and shows the presence of secondary amine. The bands observed at 2300–3500 cm^{-1} are due to the -OH stretching vibration of carboxyl, Si-OH and –NH. The stretching at 1681 cm^{-1} shows the presence of strong C=O bond representing the carboxyl group. The wavelength of 1250 cm^{-1} shows C-O-C stretching, while the stretching at 1174 cm^{-1} is due to the stretching vibration of S=O groups in polymeric chains. In addition, the adsorption bands at 780 cm^{-1} shows the presence of Si-O-Si. These peaks indicate the formation of biosilica hydrogel nanocomposites [17].



(a)



(b)



(c)

Figure.4.1. FTIR spectra (a) biosilica (b) *A. esculentus* hydrogel (AE-H) (c) Biosilica Hydrogel Nanocomposites

4.1.2. SEM Results

The SEM results are shown in Figure.4.2. The biosilica is shown in Figure 4.2 (a). The surface of hydrogel was observed to be smooth and homogeneous as depicted in Figure.4.2 (b), however, after crosslinking with biosilica, a heterogeneous pattern has been observed, Figure.4.2 (c). The irregularity in shape is attributed to use of various crosslinking agents in polymer chains.

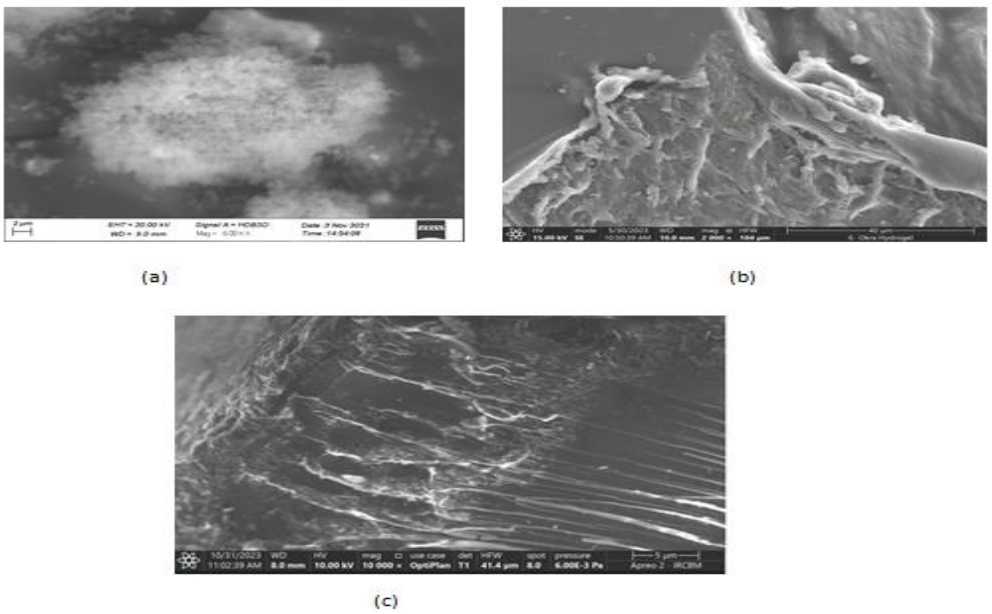


Figure 4.2. SEM images of (a) Biosilica (b) *A. esculentus* hydrogel (c) Biosilica Hydrogel Nanocomposites

4.2. Results of Phenol Removal by Silica Hydrogel Nanocomposites

4.2.1 Effect of Adsorbent Dose

The effect of the adsorbent dose on phenol removal was observed by varying the doses i.e. 0.05g/200mL, 0.1g/200mL, 0.2g/200mL, 0.4g/200mL by keeping the initial concentration10ppm for 15 minutes. The effect of the adsorbent dose on the removal of phenol from aqueous solution by silica hydrogel nanocomposites can be seen in Figure 4.3. The phenol removal was increased from 69 % to 77% as the adsorbent dose increased from 0.05g to 0.4g/200mL. It was observed that the percentage removal of phenol was increased by increasing dosage of adsorbent

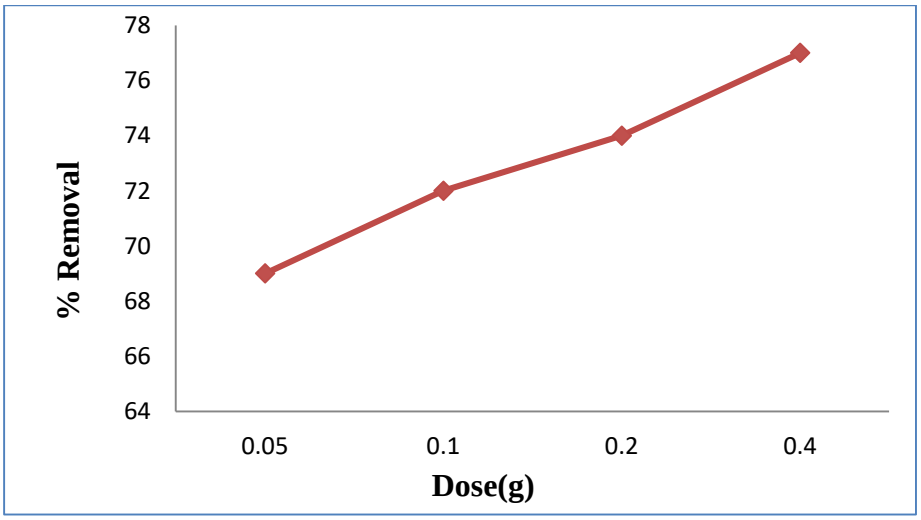


Figure 4.3. Effect of adsorbent dose on removal of phenol (Initial Conc. =10ppm, Time= 15 min)

4.2.2 Effect of initial concentration

The effect of initial concentration on removal of phenol was also found by biosilica hydrogel nanocomposites. Figure 4.4 shows the effect of initial concentration. Various initial concentrations were taken ranging from 0.5ppm to 10ppm. The results revealed that removal efficiency was enhanced by increasing the initial concentrations up to 10 ppm. It was found that phenol removal increases from 56% to 78% as initial concentration increases from 0.5 ppm to 10 ppm by using silica hydrogel nanocomposites.

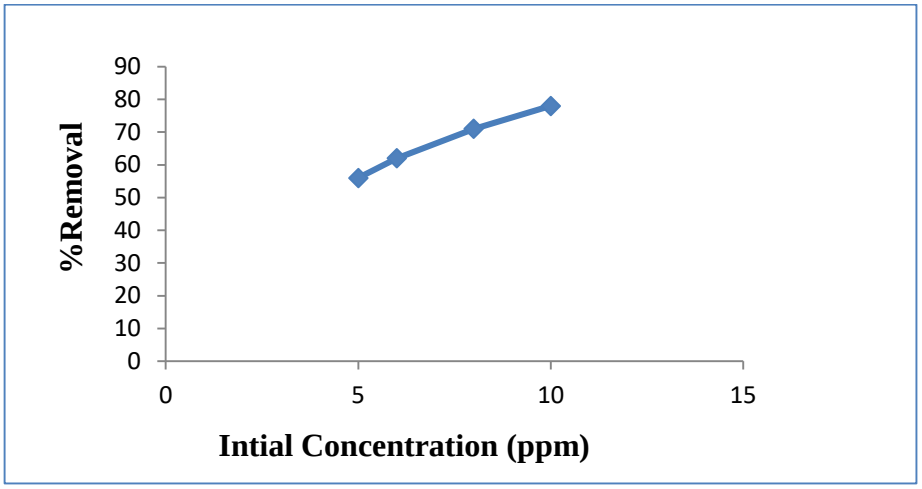


Figure 4.4 Effect of initial concentration

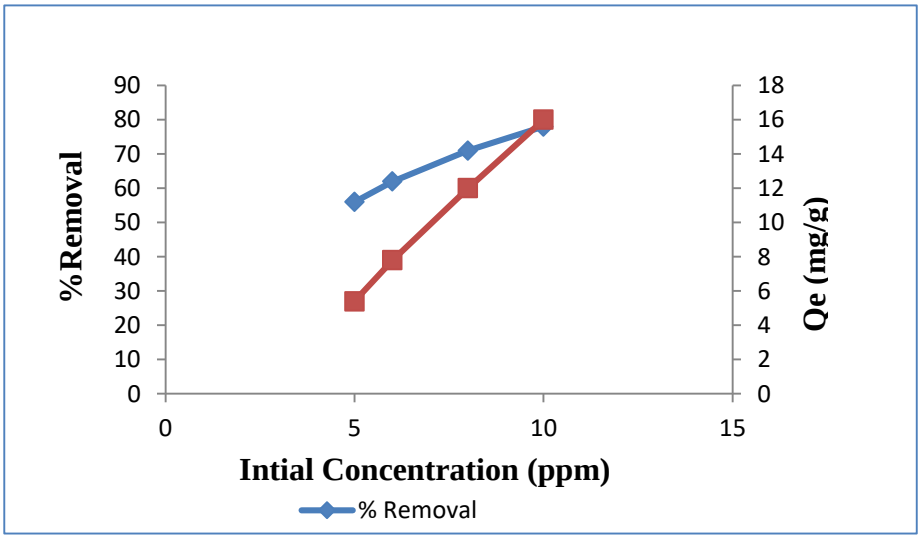


Figure 4.4. Effect of initial concentration and adsorption capacity

4.2.3 Effect of pH

The effect of hydrogen ion concentration was also examined for the adsorption of phenol at pH ranging from 2-12 with the help of biosilica hydrogel nanocomposites. Figure 4.5 shows that 78% phenol was removed at pH 7 and after that, as pH increased the removal was declined up to 61%.

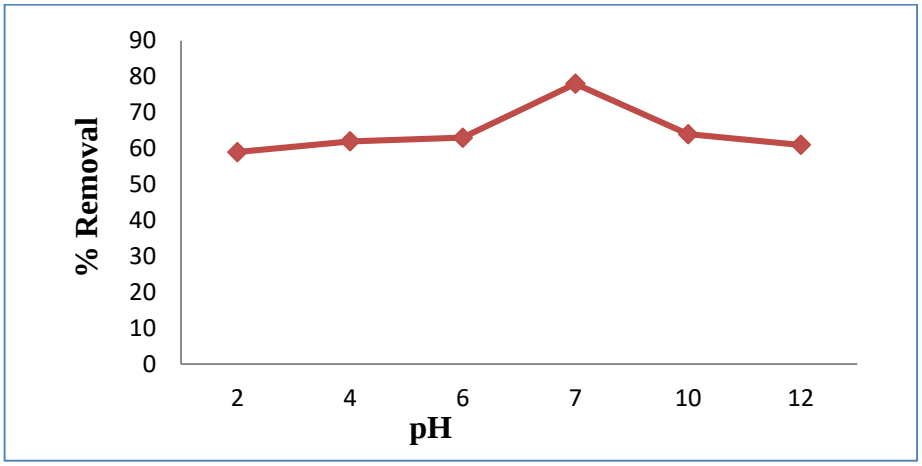


Figure 4.5.Effect of pH (Adsorbent Dose=0.4g/200ml, initial conc. = 10ppm, Time= 15 min)

4.2.4 Effect of Contact Time

The effect of contact time on phenol removal was also noticed at different contact times i.e. 15min, 30min and 90min by keeping the other parameters constant such as the adsorbent dose 0.4g, initial concentration 10ppm and pH 7. It was observed that at 15 minutes, 79% phenol was removed and then the percentage removal started to decline. It was decreased to 53% at 30 minutes and 40% at 60 minutes as shown in Figure 4.6.

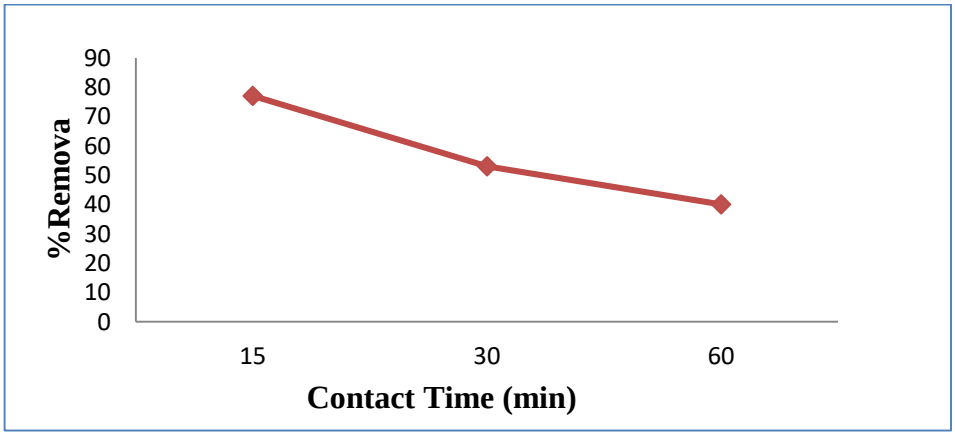


Figure 4.6. Effect of contact time on the removal of phenol (Initial Conc. =10ppm, Dose=0.4g/200mL)

4.3. Results of CV Dye removal by Silica Hydrogel Nanocomposites

4.3.1. Effect of Adsorbent Dose

The effect of the adsorbent dose on CV Dye removal was observed by varying the doses i.e. 0.025g/250mL, 0.05g/250mL, 0.1g/250mL, 0.5g/250mL by keeping the initial concentration 25 ppm for 30 minutes. The adsorption of CV dye was enhanced by 69% to 72% with the increase of doses from 0.025g to 0.1g and after that, it decreased as shown in Figure 4.7.

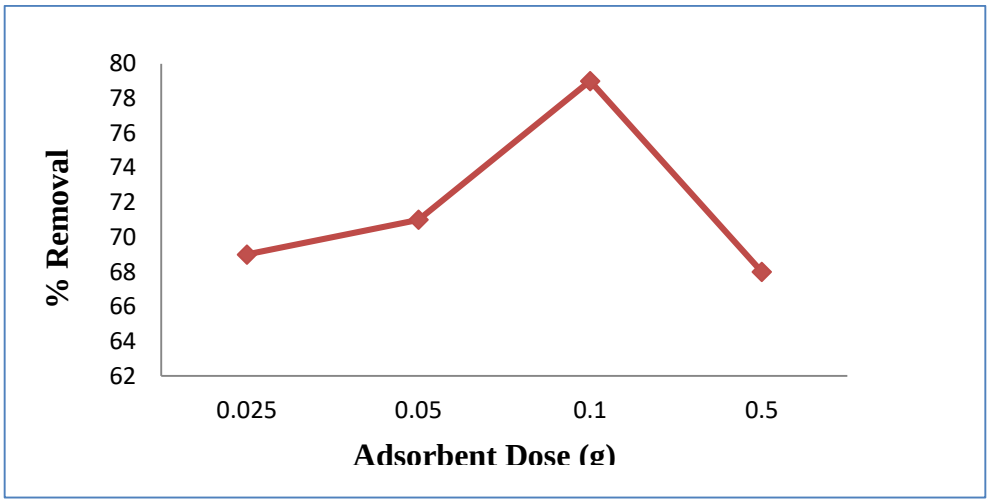


Figure 4.7 Effect of adsorbent dose on removal of CV

(Initial Conc. =25ppm, Time= 30 min)

4.3.2 Effect of initial concentration

To investigate the effect of initial concentration on the removal of CV Dye, the initial concentrations ranging from 5ppm- 30ppm were taken. It was found that the adsorption of CV was enhanced by increasing the initial concentrations to 30 ppm. It was found that dye removal increased from 51% to 75% as initial concentration increases from 5ppm to 30ppm as shown in Figure 4.8 (a).

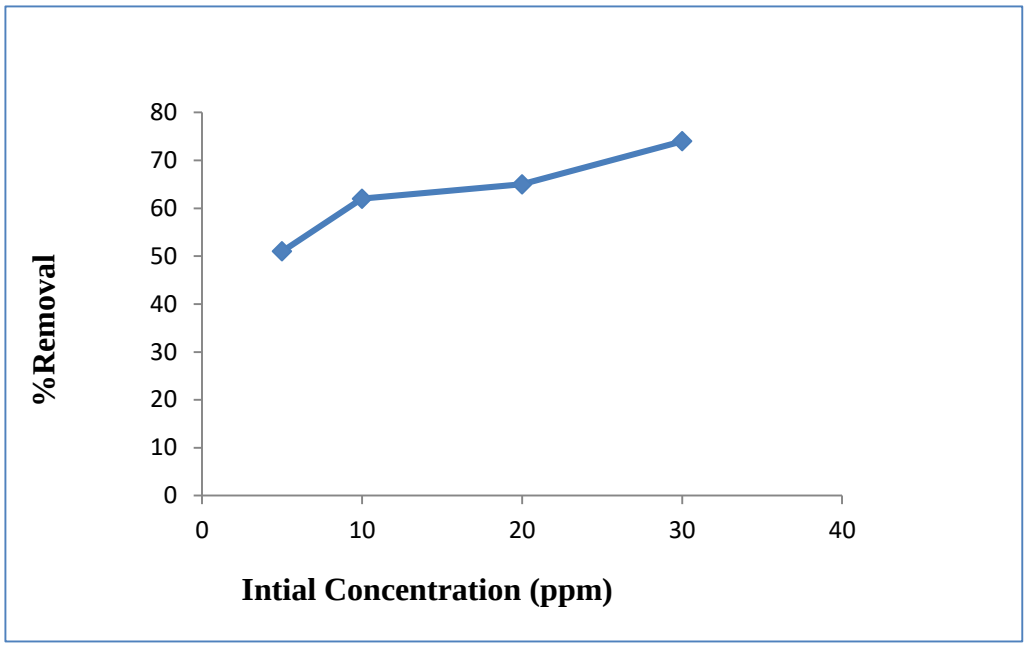


Figure 4.8. (a) Effect of concentration (Adsorbent dose= 0.1g, time= 30 minutes)

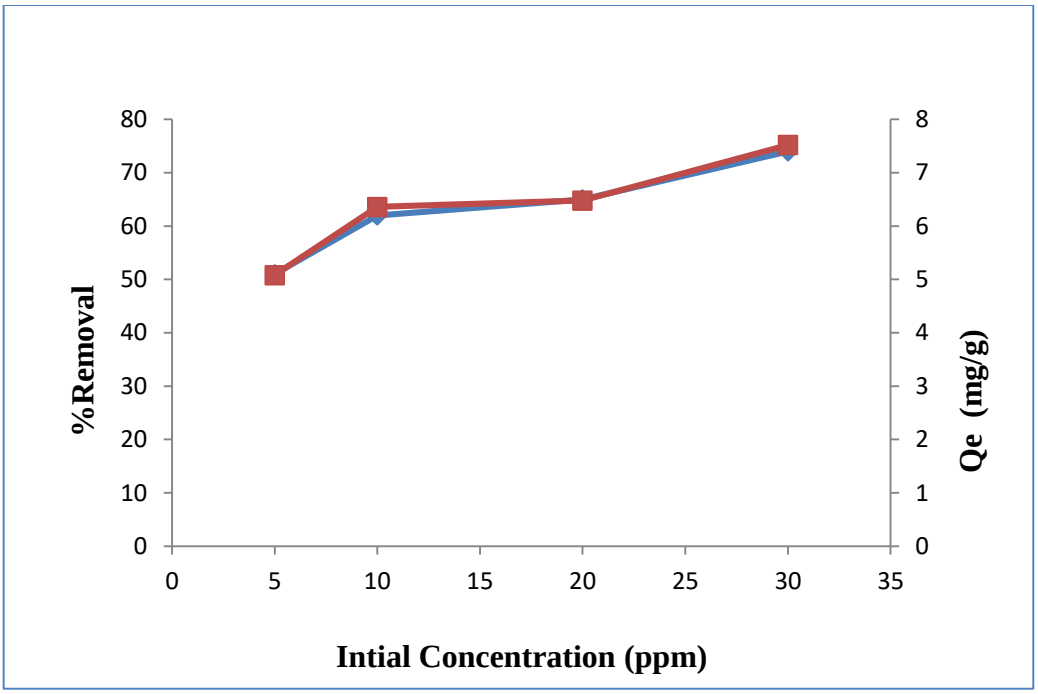


Figure 4.8. (b) Effect of initial concentration and adsorptive capacity on removal of CV (Adsorbent dose= 0.1g, time= 30 minutes)

4.3.3 Effect of pH

The effect of pH on the removal of CV Dye from aqueous solution was also observed. The maximum percentage removal of 83% at was achieved pH 12. It can be stated that percentage efficiency was less in the acidic medium and more in the basic medium as shown in Figure 4.9.

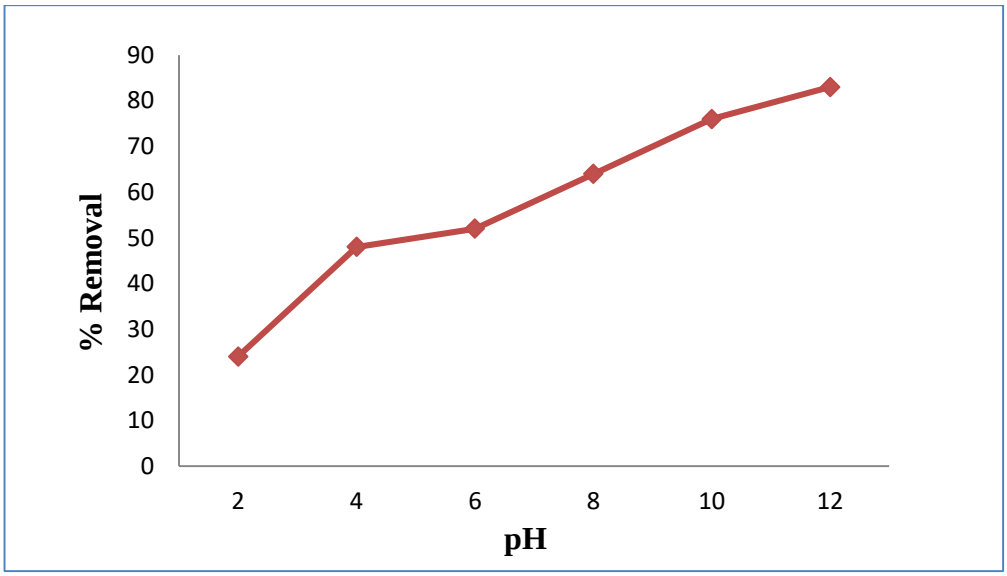


Figure 4.9. Effect of pH on removal of CV by (Adsorbent Dose=0.1, initial conc. = 25ppm, Time= 30 min)

4.3.2. Effect of Contact Time

The effect of contact time on CV adsorption was also observed at different contact times i.e. 15 min, 30 min, 60 min, 90 min and 120 min by keeping the other parameters constant such as the adsorbent dose 0.1g, initial concentration 25ppm and pH 12. It was noticed that maximum percentage removal was achieved within the first 60 minutes. The removal efficiency began was increase up to 79% and after that, it declined.

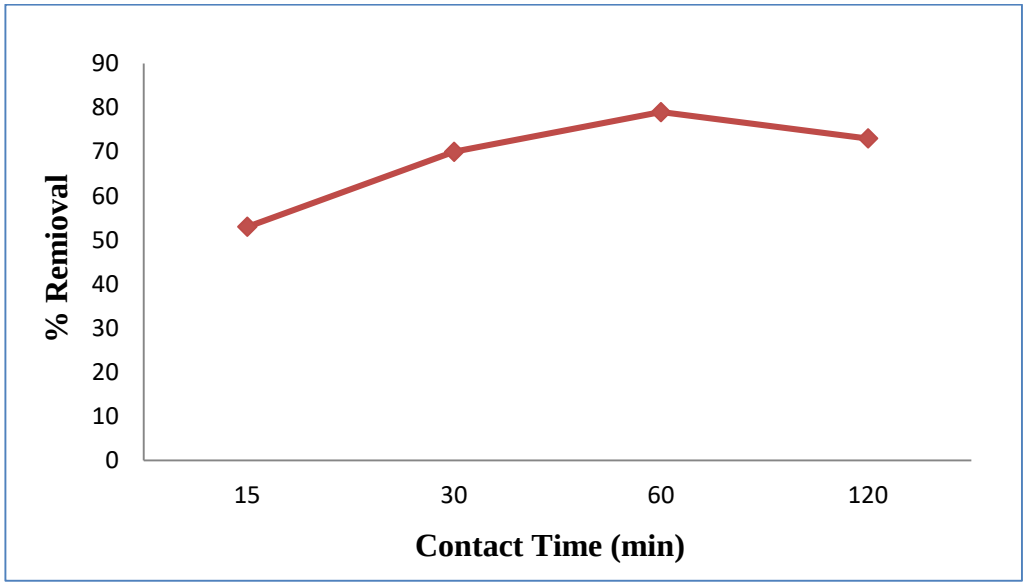


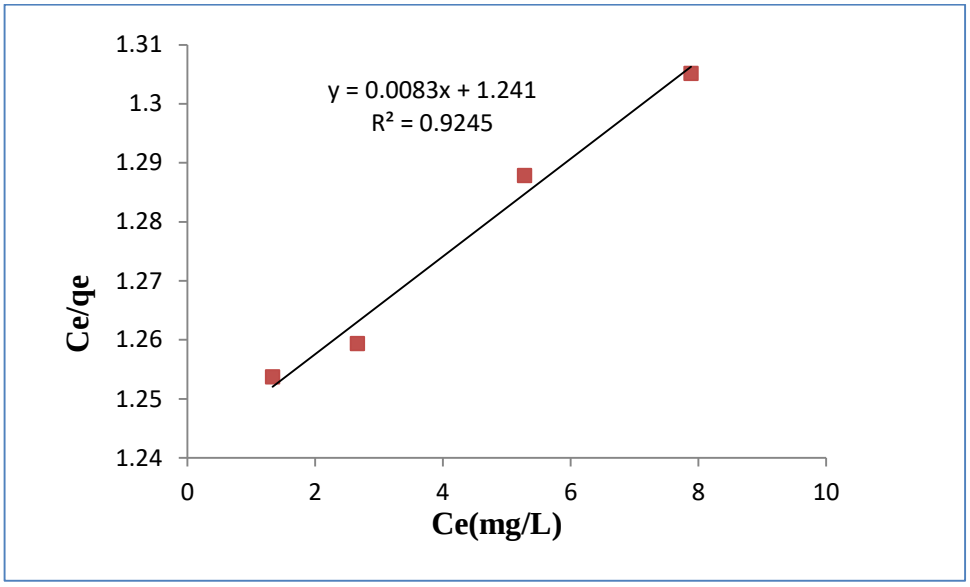
Figure 4.10. Effect of contact time on the removal of CV (Initial Conc. =25ppm, Dose=0.1g)

4.4. Adsorption isotherms

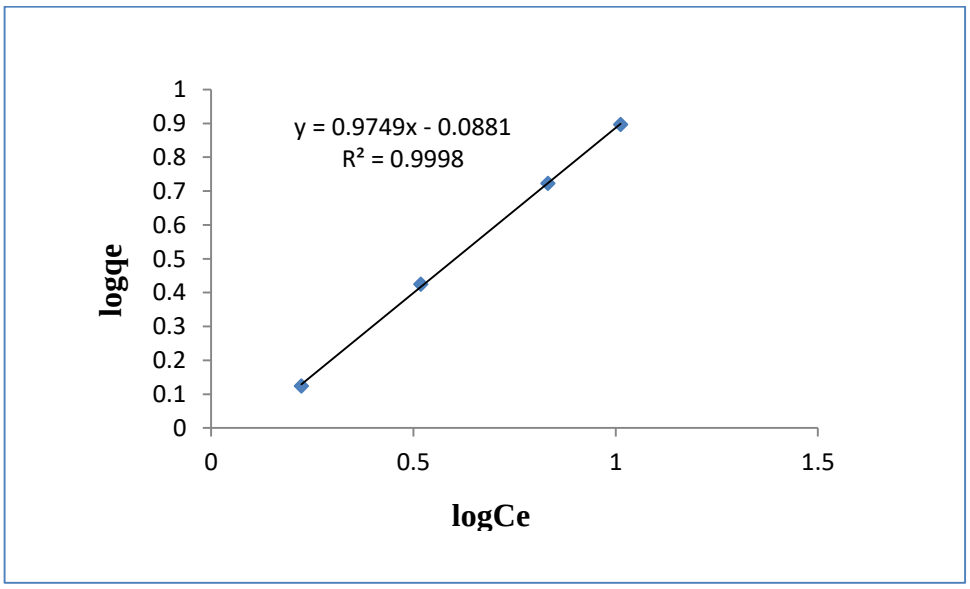
The Langmuir and Freundlich isotherm models were used to describe the interaction of adsorbate and adsorbent. The Langmuir isotherm is applicable for homogenous surfaces. The plot of Ce/q vs. Ce at various initial concentrations yielded straight lines in phenol and crystal violet, exhibited that the adsorption of phenol follows the Langmuir adsorption equation (Figure 4.11).

From the slope and intercept, the values of qm and K_L, for phenol and CV were calculated and presented in Table 4.1. The maximum adsorption capacity was 120.48 mg/g and 16.28 mg/g against CV and phenol adsorption, respectively.

Freundlich isotherm was also applied for phenol and CV adsorption by silica hydrogel nanocomposites. The values of 1/n and K_f obtained from the slope and intercept of the plot of log q_e against log C_e.

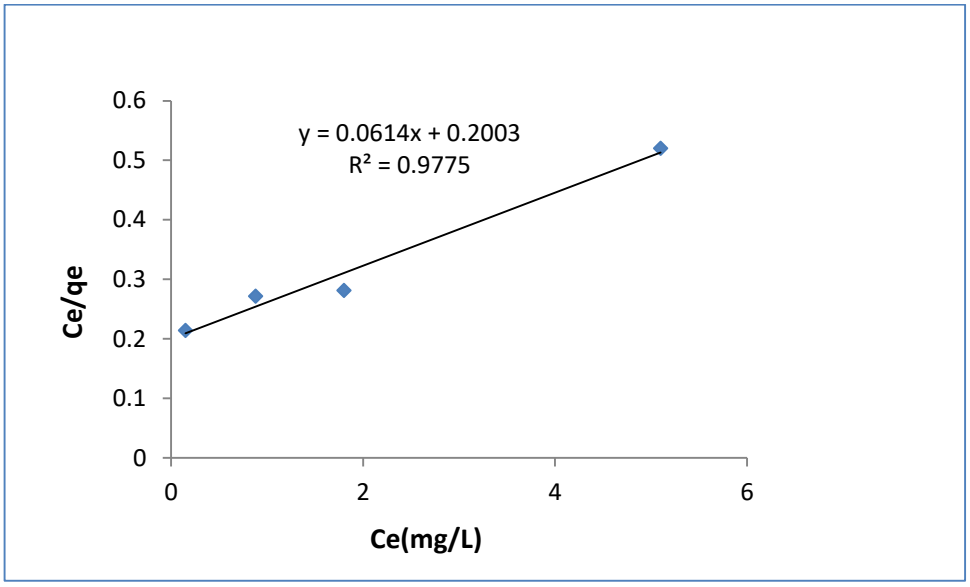


(a)

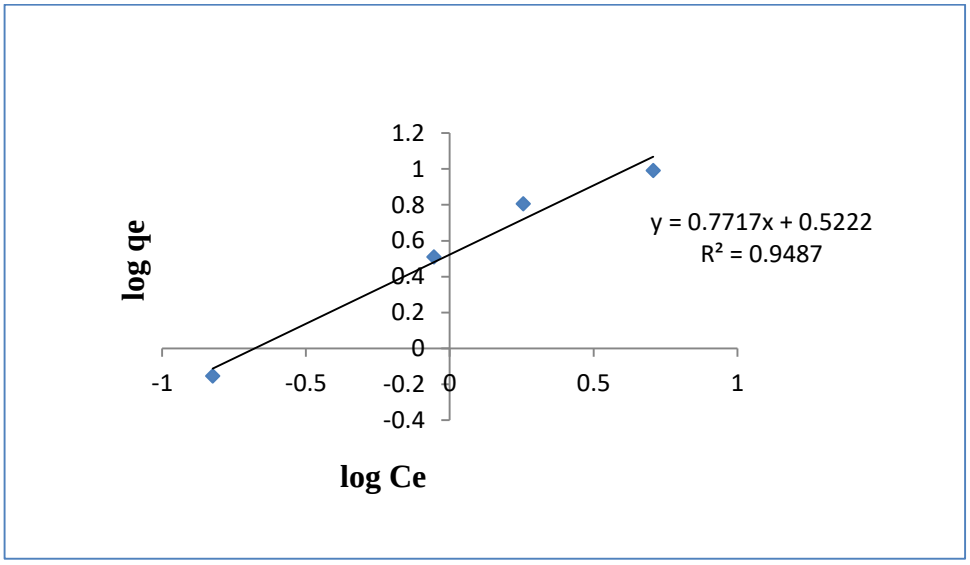


(b)

Figure 4.11. (a) Langmuir and (b) Freundlich model for CV



(a)



(b)

Figure 4.12. (a) Langmuir and (b) Freundlich model for phenol

Table 4.1 Langmuir and Freundlich isotherms parameters for phenol and CV adsorption

	Langmuir model			Freundlich model			
	q_m(mg/g)	K_L(L/mg)	R^2	1/n	n	K_f	R^2
Phenol	16.28	0.3066	0.9775	0.97	1.03	3.21	0.9487
CV	120.48	0.0078	0.9245	0.77	1.29	3.32	0.978

The parameter 1/n provides significant insights about extent of surface heterogeneity. The 1/n <1 shows that the heterogeneous nature of surface and condition 1/n>1 or 1/n=1 indicates that more homogeneous binding sites are present in sorbent. The 1/n value 0.77 in case of CV removal exhibited that surface heterogeneity and adsorption best fitted to Freundlich model. While in case of phenol removal, 1/n value is 0.97 that is very close to 1 showed that adsorbent has more homogeneous binding sites.

CHAPTER 5

DISCUSSION

Wastewater comprises human waste, food waste, solid waste, industrial discharges and detergents. It becomes extremely challenging to remove all the pollutants from the wastewater using simple techniques. These noxious substances in wastewater not only pose threats to human health but also to aquatic organisms. The crystal violet dye and phenol are among the other pollutants found in wastewater. These pollutants stand out as very toxic and persistent even in low concentrations [1]. The present study was carried out to treat two toxic pollutants i.e. phenol and crystal violet from aqueous solution using Silica Hydrogel Nanocomposites. The agricultural waste i.e. sugarcane waste and plant extract i.e. okra (*Abelmoschus esculentus*) were used for the synthesis of this adsorbent. The method employed for the synthesis of nanocomposites was conducted in the lab and proved to be very eco-friendly. Various parameters such as pH, time, dose and initial concentration were evaluated. Furthermore, the characterization of hydrogel biosilica was performed with SEM and FTIR to determine the morphology and chemical composition and compound identification.

The FTIR spectra presented in Figure 4.1 confirms the presence of biosilica hydrogel nanocomposites. These spectra Figure 4.1 (a-c) demonstrate the presence of different functional groups belonging to various organic compounds. The biosilica were analyzed through the FTIR to determine the functional groups present in prepared material. The spectrum of biosilica hydrogel nanocomposites showed a range of bonds, and stretching at various peaks. The presence of various groups such as secondary amines, alkene, carbon dioxide, nitro compounds, and sulfoynul chloride were found in biosilica shown in Figure 4.1 (a). These results are aligned with studies of Arica *et al*. [50].

The FTIR spectrum of synthesized hydrogel as shown in Figure.4.1(b) shows the presence of alcoholic groups, O=C=O bond , N=N=N groups, N=C=S bonds ,anhydride group, alkene group and N-O bonds. Similar types of bonds were observed in a study by Mishra *et al.* [51]. The FTIR spectrum of biosilica

hydrogel nanocomposites as shown in Figure 4.1 (c) showed a range of bonds, and stretching at various peaks. The presence of various groups such as secondary amines, alkene, carbon dioxide, carboxyl groups, nitro compounds were found. A study by Nakhjiri et al. [17] also confirms the presence of such bonds (e.g. alkene, carbon dioxide and silica bonds) in their study. Moreover, the morphology was further studied through the SEM showed the porous and heterogeneous nature of hydrogel nanocomposites. It also demonstrated that biosilica were well distributed in hydrogel matrix. Furthermore, the isotherm studies showed that Langmuir proved to best suited for phenol adsorption (Figure 4.11) and Freundlich proved to be appropriate for CV adsorption (Figure 4.12).

The adsorption studies of CV and phenol onto biosilica hydrogel nanocomposites are supported by various research studies. The results of crystal violet adsorption by hydrogel nanocomposites showed more removal as compared to phenol. The adsorbent doses (0.025g, 0.05g, 0.1g, 0.5g) were selected to examine the adsorption of CV with the silica hydrogel nanocomposites. It was noticed that percentage removal (%R) was increased by increasing the dose up to 0.1g. However, after %R was decreased by a further increase in dose value. The optimum value of 0.1g dose removed Crystal Violet to 72%.

The study was carried out in which crystal violet was removed from an aqueous solution using starch base hydrogel nanocomposites. The results indicated that by increasing the dose value from 0.05- 0.1g , the removal increased. The increase in adsorption by increasing the dose is due to a greater number of adsorption sites. However, the removal was reduced by further increasing the dosage value [52].

Similar trend was observed in a study in which acrylamide/graphene oxide nanocomposite hydrogel were employed for CV adsorption with adsorbent dose 0.025g-0.75g and 10 ppm solution concentration. The results exhibited that increasing the dosage up to 0.1g resulted in percentage removal up to 71% attributed to more numbers of effective groups and enhanced porosity created in configuration of hydrogel. However, further increase of dosage caused the

agglomeration of nanocomposites which reduced the penetration of CV molecules into hydrogel [53].

The other important parameter is the effect of initial concentration. It was investigated at different initial concentrations such as 5ppm, 10ppm, 20ppm, and 30 ppm by keeping the other factors constant such as 0.1g dosage and 30 minutes contact time. The results demonstrated the 74% removal of CV at 30 ppm. It means that as initial concentration was increased, removal was increased. A similar trend is noticed in a study in which clay nanocomposite hydrogels were employed for the adsorption of crystal violet. The results revealed that increasing initial concentration from 10-30mg/L, more removal of CV dye molecules was achieved. The maximum percentage removal occurred at 30mg/L [54].

In another study, the effective removal of Crystal Violet Dyes by CarAlg/MMt nanocomposite hydrogels was carried out. The adsorbent is composed of kappa-carrageenan (Car) and sodium alginate (Alg) biopolymers and sodium montmorillonite (Na-MMt). For this purpose, the initial concentration was 10-100 mg/L with 0.005g of dose. The results indicated that removal efficiency increased with increasing initial concentration up to 30 mg/L [55].

The role of pH on the adsorption of CV by biosilica hydrogel nanocomposites is also very important. The pH values were adjusted from 2 to 12 while keeping other parameters constant. The results exhibited that %R of 83% was achieved at pH 12. It can be stated that by increasing the pH value, the removal efficiency was enhanced.

This trend was supported by a study in which hydrogel comprising of biodegradable polymers was employed to degrade crystal violet dye. To find the optimum pH for CV adsorption onto the hydrogel nanocomposites, the pH range was kept from 2 to 12. The results showed that as pH increased, the [H] + ions decreased, and hence, removal increased. The maximum adsorption occurred at pH 12 [56].

Moreover, the use of multifunctionalized graphene oxide@nanopolyaniline@zirconium silicate hydrogel nanocomposite for CV removal also confirms the results. According to this research, the removal of CV was dependent on the electrostatic interaction of polar groups and the interaction of π-π bonds. The electrostatic interactions increased in an alkaline medium (pH>8) and resulted in favorable adsorption of CV dye molecules [57].

Another study in which collagen-based hydrogel nanocomposites were prepared for removal of CV supported the results. At low pH, the electrostatic attraction between the hydrogel nanocomposites decreases but at higher pH it increases [58].

In another study, Crystal Violet was removed from wastewater by using Activated Carbon/Fe_3O_4 magnetic hydrogel nanocomposite. This thermodynamic study showed that as the pH increased from 2 to 12, the adsorption of CV enhanced. As pH increases, the repulsive force between the CV dye molecules and the adsorbent surface decreases, this results in more adsorption [59]. The same trend was followed in a research study in which nanocomposite hydrogel prepared using sodium montmorillonite nanoclay was used to degrade CV. The low adsorption of CV was observed at acidic pH as excessive H+ ions compete with dye cations. As the pH increased (pH>7), the clay surface became more negative and hence, facilitated the efficient association between the adsorbent surface and dye molecules. The maximum removal efficiency was observed at high pH i.e. 12 [60]. To study the effect of Contact time on the rate of adsorption, the adsorption experiments were performed at different contact times of 15-120 minutes. The results indicated that at 60minutes the biosilica hydrogel nanocomposites removed 76% CV. Moreover, the rate of adsorption was high in with first 60 minutes after that it began to decrease.

A study in which glutathione functionalized self-assembled magnetite hydrogel nanocomposites were employed for the degradation of CV from aqueous solutions showed a percentage removal of 97% for at 60 minutes [61]. Another study in

which collagen-based hydrogel nanocomposites were synthesized for removal of CV showed maximum removal upto 75% at 60 minutes [58].

During this study, Phenol was the also removed using the biosilica hydrogel nanocomposites. The adsorbent doses (0.05g, 0.1g, 0.2g, 0.4g) were chosen to study the adsorption of phenol from aqueous solution by employing the silica hydrogen nanocomposites. It was noticed that more percentage removal was obtained at 0.4g dose. The phenol was removed upto 81% as the doses were increased. Mahmoud *et al*. [62] states that the dose of nanocomposites plays a vital role as it defines the adsorption capacity for attaining the used quantity of adsorbate. A study was carried out in which the magnetic double network nanocomposite hydrogel were prepared for removal of phenol and p-nitrophenol. The results exhibited as doses were increased from 0.01 to 0.06 g, the maximum adsorption capacity of phenol and 4-nitrophenol were increased. The reason is as doses were increased, more binding sites were formed, more electrostatic repulsion happened and hence more adsorption efficiency [63].

In another study, chitosan-carbon based hydrogel biocomposite was evaluated for treatment of phenols from aqueous solutions. The effect of various doses on the phenol adsorption was observed within the range of 10–100 mg//10 mL solutions. More removal efficiency of phenol was found by increasing the adsorbent dosage up to 70mg. It happened due to more number of active sites facilitating the adsorption of phenol molecules [64]. Similarly, the mesoporous silica nanoparticles prepared from banana peel ash was used to treat phenol. Various parameters were adjusted to check the removal efficiency of phenol. The optimum dosage value was 0.4g/L that resulted in 92.6& removal of phenol. It was observed that removal efficiency increase by increasing the dose [65].

The other significant parameter effect of initial concentration was also observed for silica hydrogel nanocomposites. Different initial concentration were prepared such as 0.5ppm, 2.5ppm, 5ppm, and 10 ppm by keeping the dosage and contact time constant i.e. 0.4g/L dosage, and 15 minutes respectively. The results showed

that by using silica hydrogel nanocomposites the removal efficiency was 79% at 10ppm. It also observed that the removal efficiency of adsorbent increased by increasing the initial concentration of phenol.

A study was conducted in which hydrogel-rice husk biochar composite was employed to degrade phenol and PNP (p-nitrophenol) from aqueous solutions. It was evident from a study that when initial concentrations were increased the phenolic removal was also increased from 67-80% [66]. Similarly, in another study was carried out in which magnetic iron oxide/carbon nanocomposites were used for adsroption of phenol. The results showed that the increase in the amount adsorbed at equilibrium was increased by increasing initial concentration of phenol [67].

The same trend was observed when the $ZnCl_2$-Activated Carbon Nanocomposites were used to remove of phenol from wastewater. The results showed that adsorption capacity was increased with an increasing initial concentration. The q_e significantly increased by increasing the initial concentration (20-100mg/L). The reason is increased phenol concentration means adding more molecules occupying the free active sites constantly and facilitated the adsorption [68].

The chitosan-carbon based hydrogel biocomposite was used for degradation of phenols from aqueous solutions. The effect of initial concentration was varied 2 to 8 mg per 10 mL of solution while dose (0.05 g) was kept constant. The results clearly indicated that 12.5% to 69% removal was achieved by varying the initial concentration of phenol from 2 to 8.0 mg per 10 mL. The results showed that more phenolic concentrations facilitate more driving forces to overcome all the mass transfer resistances of phenol [69].

In another study, the mesoporous silica nanoparticles prepared from banana peel ash was used to treat phenol. Various parameters were adjusted to check the removal efficiency of phenol. The optimum dosage value was kept 0.4g/L and initial concentration was 10 ppm that resulted in 92.6% removal of phenol. It was

observed that removal efficiency increase by increasing the initial concentration [65].

The effect of pH on phenol is a crucial factor for its adsroption on to biosilica hydrogel nanocomposites. The different pH values were adjusted from 2 to10 (2, 4, 6, 8 and 10) by keeping the dosage and contact time constant. The 0.4mg/L dosage and 15 minutes contact time were taken. It was noticed that by using adsorbent, 78% phenol was removed at 7 pH.

In a research, the graphene oxide / poly (N-isopropylacrylamide) nanocomposite hydrogel funtionlized by cyclodextrin was used to treat phenol from water. In aqueous solution, phenol is present as week acid in form of phenolate ions. In acidic medium, the potential of phenol to ionize was repressed, and as the pH is increased, phenolate ions were dominant and hence removal efficiency was enhanced. So, maximum removal was observed at pH 7. When pH was increased above 7, the electrostatic repulsion between negatively charged phenol and adsorbent decreased the phenol removal [70].

A study was conducted in which novel attapulgite nanocomposite hydrogel was used for the treatment of phenol. The pH of the aqueous solution affects the adsorption phenomenon, charge on semiconductor particles, dissociation of pollutants, and formation of aggregates. The experiments were conducted at pH range 2-12, dose 0.4g, and contact time 5-400 min. The percentage removal of phenol after was 80% pH 7. Hence, maximum removal of 81% was achieved under neutral conditions [71].

In another study, the magnetic double network nanocomposite hydrogel were synthesized for degradation of p-nitrophenol and phenol from aqueous solution. It was noticed that removal efficiency of 4-nitrophenol and phenol was 83% and 77% at pH 7 respectively [72].

Similarly, when zinc phthalocyanine/ mesoporous carbon nitride nanocomposites were used for phenol removal, the results showed that with the optimum loading

amount of 0.05 wt% ZnPc gave 61% phenol removal at pH 7 [73]. A study in which chitosan hydrogel modified with carbon nanocomposites removed the phenol from aqueous solutions also confirms the results. The study exhibited while keeping the other factors constant such as 0.025g dose, 50-400 mg/L of initial concentrations and 15 mins, the phenol removal of 88.5% at pH 7 was achieved [74]. In another study, hydrogen coated Fe_3O_4 nanoparticles were used for removing phenol from aqueous solution. The dose was increased from 0.1g/L to 0.4/L. The results showed that 92.4% removal was observed with 0.4g/L at pH 7 [75].

The effect of contact time was also observed for silica hydrogel nanocomposites. Adsorption of phenol at various contact times (15minutes, 30minutes, and 90minutes) was studied. Results showed that at first 15 minutes adsorbent showed 77% removal efficiency. After 30-60-minutes, the removal rate was decreased.

Another study supported these results in which chitosan hydrogel modified with carbon nanocomposites modified were used to remove the phenol from aqueous solutions. The results exhibited that during the initial 15 minutes while keeping the other factors constant such as 0.025g dose, 50-400 mg/L of initial concentrations and pH 7, the maximum phenol removal of 88.5% was achieved. By increasing the time, the phenol removal was decreased [74].

CONCLUSION

In this present study, the silica hydrogel nanocomposites were synthesized from the sugarcane bagasse ash and okra pods. These nanocomposites were employed for the degradation of Crystal Violet dye and phenol from aqueous solution. The SEM and FTIR analysis were used for characterization of the adsorbent which confirmed the synthesis of the silica hydrogel nanocomposites. Different batch experiments were conducted to examine the effect of various parameters such as adsorbent doses, initial concentration, pH and contact time. These experiments were conducted to evaluate the efficiency of silica hydrogel nanocomposites for the effective adsorption of phenol and crystal violet. The optimum dosage for phenol was 0.4g and for crystal violet 0.1g. For initial concentration, both the tested compounds showed the same behavior i.e. increasing the initial concentration, the RE increased. The effective initial concentration was 10 ppm and 30 ppm for phenol and crystal violet respectively. The varying pH exhibited a strong influence on the percentage removal of CV and phenol. The neutral medium i.e. pH 7 was considered as the optimum buffering solution for phenol, while pH 12 was the optimum condition for CV. Furthermore, the contact time of 15 and 30 minutes proved to be effective for phenol and crystal violet respectively. Phenol showed the removal of 79% at optimum conditions i.e. dosage 0.4 g, initial concentration 10 ppm, pH 7 and contact time 15 minutes. Crystal Violet showed the removal of 83% at optimum conditions i.e. dosage 0.1 g, initial concentration 30 ppm, pH12 and contact time 30 minutes. It can be evaluated that synthesized adsorbent proved to be more effective for the removal of crystal violet from aqueous solutions. The study confirms that silica hydrogel nanocomposites are promising adsorbent material, offering a pollutant-free alternative mechanism for the treatment of phenol and crystal violet dye from wastewater.

REFERENCES

1. Qi M, Yang Y, Zhang X, Zhang X, Wang M, Zhang W, Lu X, Tong Y. Pollution reduction and operating cost analysis of municipal wastewater treatment in China and implication for future wastewater management. Journal of Cleaner Production. 2020; 253:120003.
2. Tahir MB, Nawaz T, Nabi G, Sagir M, Khan MI, Malik N. Role of nanophotocatalysts for the treatment of hazardous organic and inorganic pollutants in wastewater. International Journal of Environmental Analytical Chemistry. 2022; 102(2):491-515.
3. Phenol Health and Safety Guide. World Health Organization. [Internet]. https://www.who.int. 1994. Available from: https://apps.who.int/iris/bitstream/handle/10665/39958/9241510889-eng.pdf;jsessionid=A9AB27D3AA50757C500967342F6B6213?sequence=1
4. Singh S, Kumar V, Romero R, Sharma K, Singh J. Applications of nanoparticles in wastewater treatment. Nanobiotechnology in bioformulations. 2019:395-418.
5. Wang Q, Shao J, Xu J, Dong F, Xiong Y, Chen Q. In-situ formed Cyclodextrinfunctionalized graphene oxide/poly (N-isopropylacrylamide) nanocomposite hydrogel as an recovery adsorbent for phenol and microfluidic valve. Journal of Colloid and Interface Science. 2022; 607:253-68.
6. Oladoye PO, Bamigboye OM, Ogunbiyi OD, Akano MT. Toxicity and decontamination strategies of Congo red dye. Groundwater for Sustainable Development. 2022:100844
7. Silva VC, Araújo ME, Rodrigues AM, Vitorino MD, Cartaxo JM, Menezes RR, Neves GA. Adsorption Behavior of Crystal Violet and Congo Red Dyes on HeatTreated Brazilian Palygorskite: Kinetic, Isothermal and Thermodynamic Studies. Materials. 2021; 14(19):5688.
8. Zahmatkesh S, Hajiaghaei-Keshteli M, Bokhari A, Sundaramurthy S, Panneerselvam B, Rezakhani Y. Wastewater treatment with nanomaterials for the future: A state-of-the-art review. Environmental Research. 2023; 216:114652.
9. Zhao F, Yao D, Guo R, Deng L, Dong A, Zhang J. Composites of polymer hydrogels and nanoparticulate systems for biomedical and pharmaceutical applications. Nanomaterials. 2015; 5(4):2054-130.

10. Thakur S, Govender PP, Mamo MA, Tamulevicius S, Thakur VK. Recent progress in gelatin hydrogel nanocomposites for water purification and beyond. Vacuum. 2017; 146:396-408
11. Seroka NS, Taziwa RT, Khotseng L. Extraction and synthesis of silicon nanoparticles (SiNPs) from sugarcane bagasse ash: A mini-review. Applied Sciences. 2022;12(5):2310.
12. Rodríguez-Díaz JM, García JO, Sánchez LR, da Silva MG, da Silva VL, ArteagaPérez LE. Comprehensive characterization of sugarcane bagasse ash for its use as an adsorbent. Bioenergy Research. 2015;8:1885-95.
13. Fard MB, Hamidi D, Yetilmezsoy K, Alavi J, Hosseinpour F. Utilization of Alyssum mucilage as a natural coagulant in oily-saline wastewater treatment. Journal of Water Process Engineering. 2021 Apr 1;40:101763.
14. Reghioua A, Barkat D, Jawad AH, Abdulhameed AS, Khan MR. Synthesis of Schiff's base magnetic crosslinked chitosan-glyoxal/ZnO/Fe3O4 nanoparticles for enhanced adsorption of organic dye: modeling and mechanism study. Sustainable Chemistry and Pharmacy. 2021; 20:100379.
15. Eltaweil AS, Elgarhy GS, El-Subruiti GM, Omer AM. Carboxymethyl cellulose/carboxylated graphene oxide composite microbeads for efficient adsorption of cationic methylene blue dye. International journal of biological macromolecules. 2020; 154:307-18.
16. Wang Q, Shao J, Xu J, Dong F, Xiong Y, Chen Q. In-situ formed Cyclodextrinfunctionalized graphene oxide/poly (N-isopropylacrylamide) nanocomposite hydrogel as an recovery adsorbent for phenol and microfluidic valve. Journal of Colloid and Interface Science. 2022; 607:253-68.
17. Nakhjiri MT, Marandi GB, Kurdtabar M. Preparation of magnetic double network nanocomposite hydrogel for adsorption of phenol and p-nitrophenol from aqueous solution. Journal of Environmental Chemical Engineering. 2021; 9(2):105039.
18. Shen J, Zhou Y, Li S, Gu P, Xue G. Hydrogel-coated Fe3O4 nanoparticles as an efficient heterogeneous Fenton catalyst for degradation of phenol. Journal of Materials Science. 2019; 54(15):10684-94.
19. Rahman MM, Al Foisal J, Ihara H, Takafuji M. Efficient removal of methylene blue dye from an aqueous solution using silica nanoparticle crosslinked acrylamide hybrid hydrogels. New Journal of Chemistry. 2021;45(43):20107-19.

20. Lahiri SK, Liu L. Fabrication of a Nanoporous Silica Hydrogel by Cross-Linking of SiO2–H3BO3–Hexadecyltrimethoxysilane for Excellent Adsorption of Azo Dyes from Wastewater. Langmuir. 2021; 37(29):8753-64
21. Santos EC, Bandeira RM, Vega ML, Santos Junior JR. Poly (melamineformaldehyde-silica) composite hydrogel for methylene blue removal. Materials Research. 2021; 24.
22. Wu L, Shi M, Guo R, Dong W. Development of a novel pullulan/polydopamine composite hydrogel adsorbent for dye removal. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2022; 652:129632.
23. Sujan MI, Sarkar SD, Sultana S, Bushra L, Tareq R, Roy CK, Azam MS. Bifunctional silica nanoparticles for simultaneous enhancement of mechanical strength and swelling capacity of hydrogels. RSC advances. 2020; 10(11):6213-22.
24. Basaleh AA, Al-Malack MH, Saleh TA. Poly (acrylamide acrylic acid) grafted on steel slag as an efficient magnetic adsorbent for cationic and anionic dyes. Journal of Environmental Chemical Engineering. 2021;9(2):105126.
25. Mohd NK, Wee NN, Azmi AA. Green synthesis of silica nanoparticles using sugarcane bagasse. InAIP conference proceedings 2017 (Vol. 1885, No. 1, p. 020123). AIP Publishing LLC.
26. Seroka NS, Taziwa R, Khotseng L. Green synthesis of crystalline Silica from Sugarcane Bagasse Ash: Physico-chemical properties. Nanomaterials. 2022; 12(13):2184.
27. Alves RH, Reis TV, Rovani S, Fungaro DA. Green synthesis and characterization of biosilica produced from sugarcane waste ash. Journal of Chemistry. 2017;2017.
28. Prasad PS, Gomathi T, Sudha PN, Deepa M, Rambabu K, Banat F. Biosilica/Silk Fibroin/Polyurethane biocomposite for toxic heavy metals removal from aqueous streams. Environmental Technology & Innovation. 2022;28:102741.
29. Kamran U, Bhatti HN, Noreen S, Tahir MA, Park SJ. Chemically modified sugarcane bagasse-based biocomposites for efficient removal of acid red 1 dye: Kinetics, isotherms, thermodynamics, and desorption studies. Chemosphere. 2022;291:132796.
30. Basaleh AA, Al-Malack MH, Saleh TA. Poly (acrylamide acrylic acid)/Baghouse dust magnetic composite hydrogel as an efficient adsorbent for metals and MB; synthesis, characterization, mechanism, and statistical analysis. Sustainable Chemistry and Pharmacy. 2021; 23:100503.
31. Singh A, Kaith BS, Mehra R, Sreejay CS, Lohan B, Bhatti MS. Synergistic effect of bio-inspired Psyllium/Okra hybrid backbone based hydrogel using RSM optimization

for efficient removal of toxic malachite green dye and sequestration of uranium (VI) ions from water.

32. Aljar MA, Rashdan S, Abd El-Fattah A. Environmentally Friendly Polyvinyl Alcohol− alginate/Bentonite Nanocomposite Hydrogel Beads as Efficient Adsorbents for Removal of Toxic Methylene Blue from Aqueous Solution.
33. Ahmad R, Ansari K. Polyacrylamide-Grafted Actinidia deliciosa peels powder (PGADP) for the sequestration of crystal violet dye: isotherms, kinetics and thermodynamic studies. Applied Water Science. 2020; 10(8):1-5.
34. Tamer Y, Berber H. Effective removal of crystal violet from aqueous solution by graphene oxide incorporated hydrogel beads as a novel bio-adsorbent: kinetic, isotherm and thermodynamic studies. Journal of Macromolecular Science, Part A. 2022; 59(4):315-28.
35. da Silva RC, de Aguiar SB, da Cunha PL, de Paula RC, Feitosa JP. Effect of microwave on the synthesis of polyacrylamide-g-chitosan gel for azo dye removal. Reactive and Functional Polymers. 2020;148:104491.
36. Cheruiyot GK, Wanyonyi WC, Kiplimo JJ, Maina EN. Adsorption of toxic crystal violet dye using coffee husks: Equilibrium, kinetics and thermodynamics study. Scientific African. 2019;5:e00116.
37. Kumar R, Ahmad R. Biosorption of hazardous crystal violet dye from aqueous solution onto treated ginger waste (TGW). Desalination. 2011;265(1-3):112-8.
38. Essekri A, Hsini A, Naciri Y, Laabd M, Ajmal Z, El Ouardi M, Ait Addi A, Albourine A. Novel citric acid-functionalized brown algae with a high removal efficiency of crystal violet dye from colored wastewaters: insights into equilibrium, adsorption mechanism, and reusability. International Journal of Phytoremediation. 2021;23(4):336-46.
39. El Naeem GA, Abd-Elhamid AI, Farahat OO, El-Bardan AA, Soliman HM, Nayl AA. Adsorption of crystal violet and methylene blue dyes using a cellulose-based adsorbent from sugercane bagasse: Characterization, kinetic and isotherm studies. Journal of Materials Research and Technology. 2022;19:3241-54.
40. Radhy ND, Jasim LS. Synthesis of graphene oxide/hydrogel composites and their ability for efficient adsorption of crystal violet. Journal of Pharmaceutical Sciences and Research. 2019 ;11(2):456-63.
41. Nguyen HT, Ngwabebhoh FA, Saha N, Saha T, Saha P. Gellan gum/bacterial cellulose hydrogel crosslinked with citric acid as an eco-friendly green adsorbent for

safranin and crystal violet dye removal. International Journal of Biological Macromolecules. 2022;222:77-89.

42. Mittal H, Al Alili A, Morajkar PP, Alhassan SM. Graphene oxide crosslinked hydrogel nanocomposites of xanthan gum for the adsorption of crystal violet dye. Journal of Molecular Liquids. 2021;323:115034.
43. Raj A, Bethi B, Sonawane SH. Investigation of removal of crystal violet dye using novel hybrid technique involving hydrodynamic cavitation and hydrogel. Journal of environmental chemical engineering. 2018;6(4):5311-9.
44. Pourjavadi A, Hosseini SH, Seidi F, Soleyman R. Magnetic removal of crystal violet from aqueous solutions using polysaccharide-based magnetic nanocomposite hydrogels. Polymer international. 2013;62(7):1038-44.
45. Lv B, Ren J, Chen Y, Guo S, Wu M, You L. Sargassum fusiforme PolysaccharideBased Hydrogel Microspheres Enhance Crystal Violet Dye Adsorption Properties. Molecules. 2022 ;27(15):4686.
46. Wang J, Zhang N, Jiang C, Zhang C. Adsorptive removal of phenol by single and double network composite hydrogels based on hydroxypropyl cellulose and graphene oxide. Journal of Materials Research. 2018;33(23):3898-905.
47. Yuney K, Oladipo AA, Gazi M, Younis DZ. CuO coated olive cake nanocomposites for rapid phenol removal and effective discoloration of high strength olive mill wastewater. Chemosphere. 2020;253:126703.
48. Mohammadi H, Kamkar A, Misaghi A. Nanocomposite films based on CMC, okra mucilage and ZnO nanoparticles: Physico mechanical and antibacterial properties. Carbohydrate polymers. 2018; 181:351-7.
49. Fahdil A, Dawood AN, Muhi FH. Kinetic and thermodynamic study on the removal of Congo red from the aqueous solution using graphene oxide/magnesium oxide nanocomposite. Journal of Biochemical Technology. 2019; 10(4):1.
50. Arica TA, Kuman M, Gercel O, Ayas E. Poly (dopamine) grafted bio-silica composite with tetraethylenepentamine ligands for enhanced adsorption of pollutants. Chemical Engineering Research and Design. 2019;141:317-27.
51. Mishra A, Nath A, Pande PP, Shankar R. Treatment of gray wastewater and heavy metal removal from aqueous medium using hydrogels based on novel crosslinkers. Journal of Applied Polymer Science. 2021;138(16):50242.
52. Moharrami P, Motamedi E. Application of cellulose nanocrystals prepared from agricultural wastes for synthesis of starch-based hydrogel nanocomposites: Efficient

and selective nanoadsorbent for removal of cationic dyes from water. Bioresource technology. 2020; 313:123661.

53. Pashaei-Fakhri S, Peighambardoust SJ, Foroutan R, Arsalani N, Ramavandi B. Crystal violet dye sorption over acrylamide/graphene oxide bonded sodium alginate nanocomposite hydrogel. Chemosphere. 2021; 270:129419.

54. Zhang Q, Zhang T, He T, Chen L. Removal of crystal violet by clay/PNIPAm nanocomposite hydrogels with various clay contents. Applied Clay Science. 2014; 90:1-5.

55. Mahdavinia GR, Aghaie H, Sheykhloie H, Vardini MT, Etemadi H. Synthesis of CarAlg/MMt nanocomposite hydrogels and adsorption of cationic crystal violet. Carbohydrate polymers. 2013; 98(1):358-65.

56. Mohamed RR, Abu Elella MH, Sabaa MW, Saad GR. Synthesis of an efficient adsorbent hydrogel based on biodegradable polymers for removing crystal violet dye from aqueous solution. Cellulose. 2018; 25:6513-29.

57. Mahmoud ME, Nabil GM, Khalifa MA, El-Mallah NM, Hassouba HM. Effective removal of crystal violet and methylene blue dyes from water by surface functionalized zirconium silicate nanocomposite. Journal of Environmental Chemical Engineering. 2019;7(2):103009.

58. Rajabi M, Mahanpoor K, Moradi O. Thermodynamic and kinetic studies of crystal violet dye adsorption with poly (methyl methacrylate)–graphene oxide and poly (methyl methacrylate)–graphene oxide–zinc oxide nanocomposites. Journal of Applied Polymer Science. 2019; 136(22):47495.

59. Mahdavinia GR, Hasanpour J, Rahmani Z, Karami S, Etemadi H. Nanocomposite hydrogel from grafting of acrylamide onto HPMC using sodium montmorillonite nanoclay and removal of crystal violet dye. Cellulose. 2013; 2591-604.

60. Kurdtabar M, Peyvand Kermani Z, Bagheri Marandi G. Synthesis and characterization of collagen-based hydrogel nanocomposites for adsorption of Cd 2+, Pb 2+, methylene green and crystal violet. Iranian Polymer Journal. 2015; 791-803.

61. Mahmoud ME, Amira MF, Seleim SM, Nabil GM, Abouelanwar ME. Multifunctionalized graphene oxide@ nanopolyaniline@ zirconium silicate nanocomposite for rapid microwable removal of dyes. Journal of Nanostructure in Chemistry. 2019; 291:651-7.

62. Foroutan R, Peighambardoust SJ, Peighambardoust SH, Pateiro M, Lorenzo JM. Adsorption of crystal violet dye using activated carbon of lemon wood and activated

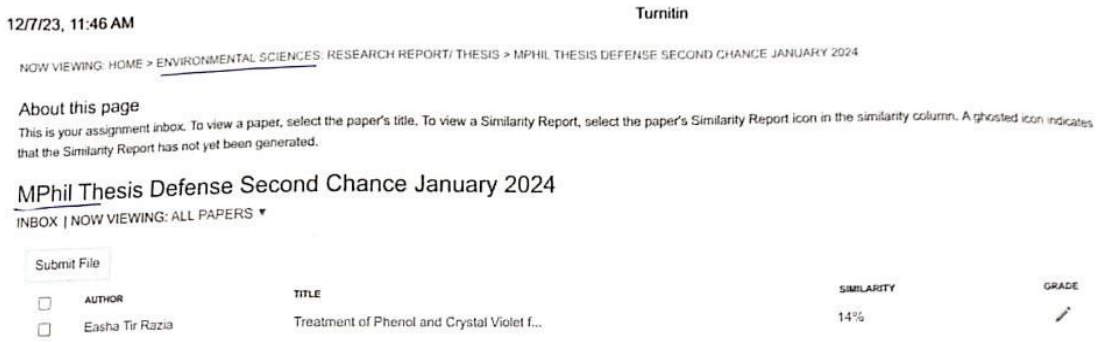
carbon/Fe3O4 magnetic nanocomposite from aqueous solutions: a kinetic, equilibrium and thermodynamic study. Molecules. 2021; 26(8):2241.

63. Behera M, Kumari N, Raza K, Singh R. Fabrication of glutathione functionalized self-assembled magnetite nanochains for effective removal of crystal violet and phenol red dye from aqueous matrix. Environmental Science and Pollution Research. 2022 (48):72260-78.
64. Saeed A, Sharif M, Iqbal M. Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption. Journal of hazardous materials.179(1-3):564-72
65. Gholami-Bonabi L, Ziaefar N, Sheikhloie H. Removal of phenol from aqueous solutions by magnetic oxide graphene nanoparticles modified with ionic liquids using the Taguchi optimization approach. Water Science and Technology. 2020; 81(2):228-40.
66. Nakhjiri MT, Marandi GB, Kurdtabar M. Preparation of magnetic double network nanocomposite hydrogel for adsorption of phenol and p-nitrophenol from aqueous solution. Journal of Environmental Chemical Engineering. 2021; 9(2):105039.
67. Soni U, Bajpai J, Singh SK, Bajpai AK. Evaluation of chitosan-carbon based biocomposite for efficient removal of phenols from aqueous solutions. Journal of water process engineering. 2017; 16:56-63.
68. Mohamad DF, Osman NS, Nazri MK, Mazlan AA, Hanafi MF, Esa YA, Rafi MI, Zailani MN, Rahman NN, Abd Rahman AH, Sapawe N. Synthesis of mesoporous silica nanoparticle from banana peel ash for removal of phenol and methyl orange in aqueous solution. Materials Today: Proceedings. 2019; 19:1119-25.
69. Sadeghi Afjeh M, Bageri Marandi G, Zohuriaan-Mehr MJ. Hydrogel-rice husk biochar composite as an adsorbent for the removal of phenol and PNP from aqueous solutions. Separation Science and Technology. 2021; 56(7):1195-210.
70. Istratie R, Stoia M, Păcurariu C, Locovei C. Single and simultaneous adsorption of methyl orange and phenol onto magnetic iron oxide/carbon nanocomposites. Arabian Journal of Chemistry. 2019;12(8):3704-22.
71. Mu'azu ND, Zubair M, Jarrah N, Alagha O, Al-Harthi MA, Essa MH. Sewage sludge ZnCl2-activated carbon intercalated MgFe–LDH nanocomposites: insight of the sorption mechanism of improved removal of phenol from water. International Journal of Molecular Sciences. 2020;21(5):1563.

72. Mohammadi L, Zafar MN, Bashir M, Sumrra SH, Shafqat SS, Zarei AA, Dahmardeh H, Ahmad I, Halawa MI. Modeling of phenol removal from water by NiFe2O4 nanocomposite using response surface methodology and artificial neural network techniques. Journal of Environmental Chemical Engineering. 2021; 9(4):105576.
73. Hosseini F, Kasaeian A, Pourfayaz F, Sheikhpour M, Wen D. Novel ZnO-Ag/MWCNT nanocomposite for the photocatalytic degradation of phenol. Materials Science in Semiconductor Processing. 2018; 83:175-85.
74. Danish EY, Bakhsh EM, Akhtar K. Design of chitosan nanocomposite hydrogel for sensitive detection and removal of organic pollutants. International journal of biological macromolecules. 2020;159:276-86.
75. Shen J, Zhou Y, Li S, Gu P, Xue G. Hydrogel-coated Fe3O4 nanoparticles as an efficient heterogeneous Fenton catalyst for degradation of phenol. Journal of Materials Science. 2019 ;54(15):10684-94.

.

PLAGIARISM REPORT



12/7/23, 11:46 AM Turnitin

NOW VIEWING: HOME > ENVIRONMENTAL SCIENCES: RESEARCH REPORT/ THESIS > MPHIL THESIS DEFENSE SECOND CHANCE JANUARY 2024

About this page

This is your assignment inbox. To view a paper, select the paper's title. To view a Similarity Report, select the paper's Similarity Report icon in the similarity column. A ghosted icon indicates that the Similarity Report has not yet been generated.

MPhil Thesis Defense Second Chance January 2024

INBOX | NOW VIEWING: ALL PAPERS ▾

Submit File

	AUTHOR	TITLE	SIMILARITY	GRADE
☐	Easha Tir Razia	Treatment of Phenol and Crystal Violet f...	14%	

For
Measiall Usman
7/12/23