METHYLENE BLUE ADSORPTION ONTO A NOVEL ADSORBENT - ISOTHERMAL STUDIES

Dissertation submitted to University of Kerala in

Partial fulfilment for the award of the degree of

MASTER OF SCIENCE IN CHEMISTRY

Submitted by

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CANDIDATE CODE: 63524142008

EXAM CODE: 63520405

COURSE CODE: CH243(a)

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KOLLAM - JULY 2026

CERTIFICATE

This is to certify that the project entitled **"METHYLENE BLUE ADSORPTION ONTO A NOVEL ADSORBENT - ISOTHERMAL STUDIES"** is a work carried out by **Ms. NOORFATHIMA N** the department of chemistry, under the guidance of **Lt. Dr. THARUN A. RAUF** submitted to the University of Kerala for the award of credits in Master in Chemistry.

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ACKNOWLEDGEMENT

I am profoundly grateful to the Almighty for providing me with the strength, perseverance, and inspiration needed to complete this project work.

I express my sincere gratitude and heartfelt thanks to Dr. Tharun A. Rauf, Assistant Professor, TKM College of Arts and Science, for his invaluable guidance, constant encouragement, constructive suggestions, and unwavering support throughout the course of this project. His expertise and insightful advice greatly contributed to the successful completion of this work.

I extend my sincere thanks to Dr. Sumalekshmi S, Head of the Department of Chemistry, for her encouragement, support, and for providing the necessary facilities to carry out this project successfully.

I am deeply grateful to Prof. Dr. M. J. Sheeba, Principal, TKM College of Arts and Science, for providing a supportive academic environment and the facilities required for the successful completion of this project.

I thank the faculty and non-teaching staff of the Department of Chemistry for their support and cooperation.

Finally, I express my heartfelt gratitude to my parents, family, and friends for their encouragement and support. Their presence and constant motivation have been a source of great strength to me.

CONTENTS

ABSTRACT

The increasing discharge of dye-containing wastewater from textile industries has become a major environmental concern due to its harmful effects on aquatic life and human health. Adsorption is considered one of the most effective and economical methods for dye removal from wastewater. In the present study, a novel cellulose-based graft copolymer composite, Cell-g-MAA/Carbon Black, was synthesized and used as an adsorbent for the removal of methylene blue dye from aqueous solution. The synthesized adsorbent was characterized to confirm successful grafting and the presence of active functional groups. Batch adsorption studies were carried out under different experimental conditions to evaluate the adsorption performance. The adsorption isotherm studies revealed that the Freundlich model best described the adsorption process, indicating multilayer adsorption on a heterogeneous surface. Thermodynamic studies showed that the adsorption was spontaneous and exothermic in nature. The results demonstrated that the synthesized composite possesses high adsorption efficiency and can serve as a low-cost, eco-friendly, and effective adsorbent for the treatment of dye-contaminated wastewater.

CHAPTER 1
INTRODUCTION

Water is an essential resource for life, yet its quality is increasingly threatened by rapid industrialization, urbanization, and agricultural activities. The discharge of untreated or partially treated effluents into water bodies introduces a wide range of contaminants, including organic pollutants, heavy metals, and synthetic dyes. These pollutants not only degrade water quality but also pose serious risks to human health, aquatic ecosystems, and overall environmental sustainability (1,2,3).

The environmental impact of dye-contaminated wastewater extends beyond aesthetic pollution. The presence of coloured compounds in water bodies affects the penetration of sunlight, thereby reducing photosynthetic activity and altering the natural ecological balance. Furthermore, several synthetic dyes and their intermediate degradation products have been reported to exhibit toxic effects toward aquatic organisms, leading to bioaccumulation and long-term environmental consequences. The increasing concern regarding the persistence of dye molecules in natural waters has stimulated extensive research into efficient and sustainable treatment technologies for their removal (4).

Among various pollutants, synthetic organic dyes are particularly problematic due to their high stability and resistance to natural degradation processes. Dyes such as methylene blue persist in aquatic environments for long periods, reducing light penetration and thereby inhibiting photosynthesis in aquatic plants. This disruption affects dissolved oxygen levels and ultimately harms aquatic life. Moreover, many dyes and their degradation products exhibit toxic, mutagenic, and even carcinogenic properties, making their removal from wastewater an urgent environmental priority (5,6,7).

The textile industry is one of the major contributors to dye pollution. While it plays a significant role in economic development, it also generates large volumes of highly contaminated wastewater. Textile processing operations—including bleaching, dyeing, printing, and finishing—require substantial amounts of water, typically ranging from

100 to 200 litres per kilogram of fabric. As a result, the effluents released contain a complex mixture of dyes, salts, surfactants, and other chemical additives (8).

Textile wastewater is widely regarded as one of the most challenging industrial effluents to treat. It is characterized by high values of chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), and suspended particles. Even trace amounts of dyes can impart intense coloration to water bodies, significantly reducing light penetration. This not only disrupts photosynthesis but also disturbs the ecological balance, posing a serious threat to aquatic organisms. Additionally, prolonged exposure to such contaminated water can adversely affect human health (6,7).

Textile effluents are highly variable in composition depending on the nature of the manufacturing process and the dyes employed. In addition to colour, these wastewaters may contain dispersing agents, surfactants, salts, acids, alkalis, and auxiliary chemicals that increase the complexity of treatment. The simultaneous presence of multiple contaminants often reduces the efficiency of conventional treatment methods and necessitates the development of advanced purification strategies capable of removing diverse classes of pollutants (8,4).

Among the various dyes used in textile industries, methylene blue has gained considerable attention in environmental research. It is a cationic dye widely used in dyeing cotton, silk, and wool, as well as in biological staining and certain medical applications. Despite its utility, methylene blue becomes a serious pollutant when released into water systems. Its resistance to biodegradation allows it to persist in the environment, and exposure to contaminated water can lead to health issues such as eye irritation, respiratory problems, and toxicity to aquatic organisms. Due to its well-defined structure and intense colour, methylene blue is frequently used as a model pollutant to evaluate the efficiency of wastewater treatment methods.

The treatment of dye-containing wastewater is particularly difficult due to the chemical stability and complex structure of synthetic dyes. Conventional treatment methods such as coagulation–flocculation, biological degradation, and chemical oxidation can partially reduce pollutant levels; however, they often fail to achieve complete colour removal. These methods may also involve high operational costs, significant energy consumption, and the generation of secondary pollutants such as sludge, which require

further treatment and disposal (6,7,8). Furthermore, many synthetic dyes present in textile effluents are recalcitrant in nature and exhibit low biodegradability, making their complete removal difficult through conventional treatment processes alone. Consequently, hybrid treatment approaches combining adsorption with advanced oxidation techniques have attracted increasing attention due to their enhanced efficiency in colour removal and pollutant mineralization. (4).

In this context, adsorption has emerged as one of the most effective and widely used techniques for dye removal from aqueous systems. Adsorption is a surface phenomenon in which pollutants accumulate on the surface of a solid material known as an adsorbent. This method is highly favoured due to its simplicity, cost-effectiveness, flexibility, and high efficiency, especially in removing low concentrations of contaminants. Unlike absorption, which involves bulk penetration, adsorption is governed by surface interactions such as van der Waals forces, electrostatic attraction, and chemical bonding (5,3,7).

Adsorption has attracted considerable attention because of its operational simplicity and ability to remove contaminants even at low concentrations. Compared with many conventional treatment processes, adsorption does not generally produce harmful by-products and can be implemented using a wide range of naturally available or synthetically prepared adsorbent materials. These advantages have established adsorption as one of the most versatile technologies for wastewater purification (3,5).

The mechanism of adsorption can be broadly classified into physisorption and chemisorption. Physisorption involves weak intermolecular forces and is generally reversible, whereas chemisorption involves the formation of stronger chemical bonds and is often irreversible. In many dye removal processes, both mechanisms may occur simultaneously, depending on the nature of the adsorbent and the functional groups present on its surface (3).

A wide variety of adsorbents have been investigated for dye removal, including activated carbon, natural clays, agricultural wastes, and synthetic polymers. Although activated carbon is highly effective due to its large surface area and porosity, its high cost and regeneration limitations have prompted the search for alternative materials. In recent years, polymer-based adsorbents, particularly those containing functional groups such as carboxyl (-COOH), have attracted significant attention. These functional groups

enhance adsorption by facilitating interactions such as electrostatic attraction, hydrogen bonding, and ion exchange (1,3,7).

The adsorption capacity of polymeric materials can be significantly improved through chemical modification. The introduction of functional groups onto polymer chains increases the number of active adsorption sites and enhances interactions with target pollutants. Such modifications allow the development of tailor-made adsorbents with improved selectivity, stability, and adsorption performance for specific environmental applications (9).

In the case of methylene blue, which carries a positive charge, adsorbents with negatively charged functional groups—such as carboxyl groups—exhibit strong affinity toward the dye molecules. This interaction significantly improves adsorption efficiency, making such materials highly suitable for wastewater treatment applications. The adsorption behaviour of cationic dyes is strongly influenced by the surface chemistry of the adsorbent. Functionalized adsorbents containing ionizable groups can provide selective binding sites for dye molecules, thereby enhancing adsorption capacity and improving removal efficiency from aqueous solutions (10).

One of the most promising approaches in this field is the development of graft copolymers. Graft copolymerization involves the attachment of side chains onto a polymer backbone, allowing the incorporation of functional groups that enhance the material's properties. This structural modification improves adsorption capacity, selectivity, and stability, enabling the design of materials tailored for specific pollutants (9).

The adsorption behaviour of cationic dyes is strongly influenced by the surface chemistry of the adsorbent. Functionalized adsorbents containing ionizable groups can provide selective binding sites for dye molecules, thereby enhancing adsorption capacity and improving removal efficiency from aqueous solutions (11).

Polymethyl methacrylate (PMMA) is a widely used synthetic polymer known for its excellent optical clarity, mechanical strength, and chemical resistance. However, its relatively inert nature and lack of active functional groups limit its direct application in adsorption processes. To overcome this limitation, graft copolymerization is employed to introduce reactive groups onto the PMMA backbone, thereby enhancing its surface activity and adsorption potential.

Graft copolymerization is typically carried out using free radical polymerization techniques, where reactive sites are generated on the polymer backbone using initiators such as potassium persulfate. These active sites enable the attachment of monomer units, forming grafted chains. The efficiency of this process depends on factors such as temperature, initiator concentration, and reaction time, which influence the degree of grafting and the final properties of the material (9).

The incorporation of functional monomers containing carboxyl groups (-COOH) plays a crucial role in enhancing adsorption performance. These groups introduce negatively charged sites on the polymer surface, enabling strong interactions with positively charged dye molecules through electrostatic attraction and ion-exchange mechanisms. This functionalization significantly improves the applicability of graft copolymers in aqueous systems (9).

Further enhancement in material performance can be achieved by developing hybrid inorganic–organic composites. The incorporation of inorganic components such as clay minerals into polymer matrices results in materials with improved surface area, porosity, thermal stability, and mechanical strength. These composites provide additional active sites and better dispersion of functional groups, thereby enhancing adsorption efficiency (1,9).

Hybrid organic–inorganic materials have emerged as promising adsorbents due to the synergistic combination of the flexibility of polymers and the structural stability of inorganic components. The incorporation of inorganic phases often enhances mechanical strength, thermal stability, and surface characteristics, resulting in materials that exhibit improved adsorption behaviour compared with their individual constituents (9).

Such hybrid graft copolymers also exhibit desirable properties such as pH responsiveness, high swelling capacity, and reusability, making them particularly suitable for wastewater treatment applications. The synergistic interaction between the organic polymer and inorganic filler contributes to improved adsorption behaviour and structural stability.

Characterization of the synthesized graft copolymer is essential to confirm successful grafting and to understand its physicochemical properties. Techniques such as Fourier Transform Infrared Spectroscopy (FTIR) are used to identify functional groups and

confirm chemical bonding, while Scanning Electron Microscopy (SEM) provides information on surface morphology and porosity. Additionally, surface area analysis using the BET method helps evaluate the adsorption potential of the material. These characterization techniques establish a clear relationship between the structure and functionality of the synthesized copolymer (9,12).

Among the various characterization techniques, FTIR spectroscopy is particularly useful for identifying functional groups and confirming successful grafting or chemical modification. X-ray diffraction analysis provides information regarding the crystalline or amorphous nature of the synthesized material, while thermogravimetric analysis offers valuable insight into thermal stability and decomposition behaviour. Together, these techniques facilitate a comprehensive understanding of the structure–property relationship of adsorbent materials (11).

To evaluate adsorption performance, equilibrium studies are conducted using adsorption isotherms such as the Langmuir and Freundlich models. The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface with identical binding sites, while the Freundlich isotherm describes adsorption on heterogeneous surfaces with varying site energies. Kinetic studies, including pseudo-first-order and pseudo-second-order models, are also important in understanding the rate and mechanism of adsorption. In many cases, dye adsorption follows pseudo-second-order kinetics, indicating that chemisorption plays a significant role.

In addition to kinetic modelling, diffusion studies are often employed to investigate the rate-controlling steps involved in adsorption. The transport of adsorbate molecules from the bulk solution to the adsorbent surface may occur through film diffusion, pore diffusion, or a combination of both mechanisms. Understanding these transport processes is important for optimizing adsorption systems and improving overall treatment efficiency (11).

Thermodynamic studies further reveal the nature of the adsorption process, which is often spontaneous and may be either exothermic or endothermic depending on the system. These analyses are essential for optimizing adsorption conditions and improving material performance.

In summary, the increasing environmental impact of textile wastewater necessitates the development of efficient and sustainable treatment methods. The persistence and

toxicity of dyes such as methylene blue highlight the urgent need for advanced purification strategies. Among the available methods, adsorption—particularly using functionalized polymeric materials—offers a highly effective and eco-friendly solution.

This forms the foundation of the present study, which focuses on the synthesis and characterization of a novel graft copolymer containing carboxyl groups and its application in the removal of methylene blue from aqueous media.

CHAPTER 2

LITERATURE REVIEW

The increasing demand for clean water and the growing generation of industrial wastewater have encouraged extensive research on efficient and sustainable treatment technologies. Adsorption has emerged as one of the most effective and economical methods for wastewater remediation due to its simplicity, high efficiency, and environmental compatibility.

Shannon et al. (2008) discussed the global water crisis and emphasized the need for advanced water purification technologies, including water disinfection, decontamination, wastewater reuse, and desalination, to ensure sustainable access to safe drinking water. (13)

Ali, Asim and Khan (2012) reviewed the use of low-cost adsorbents for wastewater treatment and reported that agricultural wastes, industrial by-products, fruit wastes, rice husks, fly ash, zeolites, and clays can effectively remove pollutants from water. The study highlighted adsorption as an economical and highly efficient treatment technique. Ali et al. (2012) also noted that although activated carbon is highly effective, its high cost has encouraged the development of alternative adsorbents derived from waste materials. (14)

Akeremale (2022) reviewed the application of Metal–Organic Frameworks (MOFs) for dye-contaminated wastewater treatment. The study reported that MOFs possess high surface area, tunable pore structures, and excellent adsorption capacities, making them promising adsorbents for dye removal. The author further emphasized that adsorption remains a preferred treatment method because of its simplicity, cost-effectiveness, and environmental friendliness. (5)

Liu et al. (2025) reviewed industrial waste-based adsorbents and reported that materials such as red mud, steel slag, fly ash, and paper mill sludge can be modified to enhance pollutant removal. Physical and chemical treatments including calcination, acidification, and chemical doping were found to increase surface area and active adsorption sites. (1)

Supporting these findings, Yang et al. (2020) demonstrated that calcined red mud showed improved adsorption of cadmium ions due to increased surface area and additional hydroxyl groups, while Li et al. (2006) reported enhanced phosphate adsorption after red mud calcination. (1)

The treatment of textile wastewater has received considerable attention because textile effluents contain large amounts of dyes and organic pollutants. Himanshu Patel and R.T. Vashi (6) investigated adsorption and coagulation methods for textile wastewater treatment. Using activated charcoal, they achieved significant reductions in COD, BOD, and color, demonstrating the effectiveness of adsorption-based treatment.

Najah M. Al-Shuwaiki, Balasim A. Abid, and Mahmood M. Brbooti (15) studied color removal from textile wastewater using magnesium oxide and calcium oxide. Their results showed removal efficiencies above 95% under optimized conditions, indicating the effectiveness of these materials as adsorbents and coagulants.

K. Senthilkumar, V. Chitra Devi, S. Mothil, and M. Naveen Kumar (7) evaluated marine sediment (natural clay) as a low-cost adsorbent for textile effluent treatment. The adsorption process followed pseudo-second-order kinetics and fitted the Langmuir isotherm model, confirming the potential of natural clay for wastewater treatment.

Advanced treatment technologies were explored by Hua Yin, Peiwen Qiu, Yuange Qian, Zhuwen Kong, Xiaolong Zheng, Zhihua Tang, and Huafang Guo (8), who developed a treatment system combining ozonation, ultrafiltration, and reverse osmosis. The integrated process effectively removed color, COD, and dissolved salts, producing water suitable for reuse.

Cellulose-based materials have attracted considerable interest as adsorbents due to their abundance, biodegradability, and ease of modification. Hashem, Sokker, Abdel Halim and Gamal (2005) investigated the grafting of itaconic acid onto cellulosic fabric waste for methylene blue removal. The modified adsorbent showed enhanced adsorption performance with a maximum adsorption capacity of 38 mg g^{-1}. The study demonstrated that introducing carboxylic acid groups significantly improved dye adsorption efficiency. (12)

Jayasantha Kumari, Krishnamoorthy, Arumugam, Radhakrishnan and Vasudevan (2016) developed a Typha latifolia activated carbon/chitosan composite for crystal

violet removal from wastewater. The composite exhibited adsorption efficiencies close to 99% and followed Langmuir, Freundlich, and pseudo-second-order kinetic models. The study highlighted the role of chitosan in enhancing adsorption capacity through the introduction of additional active binding sites. (16)

The application of polymer-grafted cellulose composites for heavy metal and radioactive ion removal has also been extensively investigated. Anirudhan, Tharun, Rijith and Suchithra (2011) synthesized a poly(methacrylic acid)-grafted cellulose/bentonite superabsorbent composite for uranium(VI) removal. More than 99% uranium removal was achieved, and the adsorbent demonstrated excellent regeneration and reusability characteristics. (3)

Similarly, Anirudhan, Suchithra, Senan and Tharun (2012) studied the adsorption of thorium(IV) ions using poly(methacrylic acid)-grafted cellulose/bentonite composite. The adsorbent achieved over 99.7% thorium removal and exhibited a maximum adsorption capacity of 188.1 mg g^{-1}, indicating its suitability for radioactive wastewater treatment. (9)

Theoretical understanding of adsorption has also contributed significantly to adsorbent design. P.-G. de Gennes (17) developed the scaling theory of polymer adsorption and explained the influence of polymer chain length, solvent quality, and surface interactions on adsorption behavior. This work provided an important theoretical basis for the development of polymer-based adsorbents.

Further advancements in functionalized cellulose adsorbents were reported by Thayyath Sreenivasan Anirudhan, Sylaja Raveendran Rejeena, and Abdul Rauf Tharun (18), who synthesized a tannin-modified polymer-grafted cellulose adsorbent for selective bovine serum albumin separation. The adsorbent exhibited an adsorption efficiency of approximately 97.8%, demonstrating the effectiveness of polymer grafting in improving adsorption performance.

Likewise, Thayyath Sreenivasan Anirudhan and Sylaja Raveendran Rejeena (19) developed a polymer-grafted magnetite nanocellulose composite for hemoglobin adsorption. The composite showed a high adsorption capacity of 248.19 mg/g and enabled easy magnetic separation due to the incorporation of magnetite nanoparticles.

In the context of sustainable resource utilization, M. P. Todor, C. Bulei, T. Heput, and I. Kiss (20) investigated biodegradable composites reinforced with natural textile fibers and recycled textile waste. The study highlighted the environmental benefits of replacing synthetic reinforcements with renewable fibers.

Similarly, Irena Wojnowska-Baryła, Katarzyna Bernat, Magdalena Zaborowska, and Dorota Kulikowska (21) reviewed textile waste management practices and emphasized the importance of recycling, reuse, and circular economy approaches to reduce the environmental burden associated with textile waste disposal.

CHAPTER 3

EXPERIMENTAL METHODS

Materials

The whole chemicals and reagents used for experimental process and analysis were of analytical grade and were used as such. All stock solutions were prepared using double distilled water. Cellulose was purchased from Fluka Chemie (Buchs, Switzerland). Methacrylic Acid (MAA, 98%), Methylene Bis Acrylamide (MBA99%), $K_2S_2O_8$ (98%), and sodium bicarbonate were obtained from E. Merck India. Sodium dithiocarbamate (99%) was purchased from Sigma-Aldrich (Sigma, St. Louis, MO). A stock solution of 1000 mg/L of Methylene Blue (MB) was prepared by dissolving accurately weighed MB, (Fluka, Switzerland) in distilled water. Working solutions were prepared by diluting the stock solution.

Synthesis of Cell-g-MAA/Carbon Black composite

About 6 g MAA , 1.0 g Cellulose, 0.25 g Carbon Black and 20 mL of water is mixed and placed in a Hot Plot having magnetic stirrer. After 10 minutes of stirring, 0.15 g of MBA and 0.20 g of $K_2S_2O_8$ was added. The polymerization temperature was set at 70°C for 4 h to ensure complete consumption of the monomer. On completion of polymerization reaction, 1.5-g sodium bicarbonate was added that acts as a porogen, which prevents the hardening of the grafted polymer. The grafted polymer composite was then filtered and washed several times with ethanol to remove any unreacted monomers and homopolymers. Washing with ethanol will remove the dissolved homopolymer and water from the surface of the product. The product was then dried in an air oven by keeping the temperature at 50°C for 4 h. The dried sample was ground and sieved to obtain 80 ± 230 mesh size of particles (average diameter of 0.096 mm). The concentration of the carboxylic acid groups in the graft copolymer was determined by acid–base titration method. The carboxylic acid groups of Cell-g-PMAA/Carbon Black were first treated with HCl for the recovery of COOH groups, which might be in basic nature on treatment with Na_2CO_3. Thus, treated composite was then neutralized with a known excess of NaOH, and their unreacted NaOH was titrated with HCl. The concentration of the carboxylic acid groups was determined as follows:

[COOH]= $V_{NaOH}C_{NaOH}$ -V_{HCl} _C_{HCl}, where V_{HCl} C_{HCl} is the amount of HCl used during titration.

Adsorption experiments

Adsorption experiments were carried out in thermostated water bath shaker at 30°C with a shaking speed of 200 rpm using 100 Erlenmayer flasks. Batch experiments were performed by equilibrating 0.05 g of adsorbent with 50 mL MB solutions of predetermined initial concentrations. The initial pH of the solutions was maintained at 6 by adding 0.1M NaOH and HNO_3. The suspensions were shaken for 4 h.

Measurements

The spectrophotometric determination of the concentration of MB in solution was done on a Jasco UV-visible (model V-530, India) spectrophotometer by measuring absorbance at λ_{max} of 640 nm.

CHAPTER 4

RESULTS AND DISCUSSION

Synthesis and characterization of the adsorbent

Graft copolymerization of the MAA onto the cellulose backbone was carried out in a homogenous system using $K_2S_2O_8$ as a radical initiator and MBA as a crosslinking agent. The mechanism involved in the graft copolymerization of MAA/MBA onto Cell using the said initiator system has been proposed by earlier workers. These anionic radical abstracts hydrogen from hydroxyl group of the cellulose to form the Cell macroradicals. In the presence of vinyl monomer, the Cell macroradical is added to the double bond of the monomer resulting in a covalent bond between the monomer and the Cell with creation of a free radical on the monomer, i.e., a chain is initiated. The homopolymerization reaction may be favoured by the radicals such as H and/or OH formed. Since a crosslinking agent (MBA) is present in the system, a polymer network is formed with free COOH groups at the chain length. The Carbon black particles in the network enhance the swelling ability and mechanical strength. The degree of MAA grafting on the composite was found to be 61.0%, which is much greater than that of the reported values. The amount of carboxylic acid groups in Cell-g-PMAA/Carbon black was found to be 1.91 meq/g.

Adsorption Studies

Different types of Carbon black were available as fillers and adsorption conducted in such a manner that, UV studies (concentration) were conducted before and after adsorption. The studies are shown below. Studies onto MB was conducted on a particular concentration with respect to the various types. The concentration of MB was fixed on 300 ppm and the different types of carbon blacks were N133, N134, N139 and N140. The different types were based on its pore size. The adsorptive studies were

Types of Carbon Black	Before adsorption	After adsorption	Percentage of adsorption
N133	0.6945	0.0081	98
N134	0.6945	0.0067	99
N139	0.6945	0.0282	95
N140	0.6945	0.0381	94

These values suggest that the type N134 is showing better result than the others. It's basically due to the difference in pore size and correspondingly due to increase in surface area. The surface area is optimized for N133 adsorption studies were further conducted by incorporating this selected carbon black.

Adsorption Isotherm

For the optimization of the adsorption mechanism, the application of adsorption isotherms was very useful in describing the interaction between the adsorbent and the adsorbate. For the formulation of adsorption mechanism, the experimental isotherm data interpretations were done by the non-linear forms of isotherm models. Generally for single solute systems Langmuir and Freundlich isotherm models were used. But here various isotherm models were employed in order to explain a suitable adsorption mechanism. Hence in this work, isotherm models of two parameters (Freundlich, Langmuir, and Temkin) [22] and three parameters (Redlich-Peterson, Sips) were applied [23]. The listed equations with the explanation of parameters are shown in Table 1. Freundlich adsorption isotherms assumes that the adsorption is occurring in a heterogenous surface, while Langmuir isotherm model suggest the adsorption process in an ideal condition which meant that the adsorption process will be occurring in homogenous surface only. Temkin isotherm is generally related with the adsorption heat generated by the molecules due to the interaction between the adsorbates. The Redlich-Peterson isotherm was generated in order to find out the correlation between the

Langmuir and Freundlich isotherm models. The Sips isotherm is a combination of Freundlich and Langmuir isotherm models. This isotherm model explains the fact that at higher concentration the adsorption favors Langmuir and at lower concentration the adsorption favors Freundlich.

Table 1

The isotherm models (nonlinear forms) that have been employed for studying the adsorption process: Two parameter models (Langmuir, Freundlich, Temkin) and three parameter models (Sips, Redlich-Peterson)

Isotherm	Equation	Parameters
Langmuir	$q_e = \frac{q_m b C_e}{1 + b\ C_e}$	C_e (mg/L) is the equilibrium concentration, b is Langmuir constant, and q_m(mg/g) is the maximum adsorption capacity
Freundlich	$q_e = K_F C_e^{1/n}$	K_F (L/mg), n are the Freundlich constants
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	R is the universal gas constant and b(J/mol), K_T(L/mg) are Temkin constants
Sips	$q_e = \frac{q_S K_S C_e^{n_S}}{1 + K_S C_e^{n_S}}$	q_s(mg/g) is the maximum adsorption capacity, K_S, n_s are the Sips constants
Redlich Peterson	$q_e = \frac{K_{RP} C_e}{1 + b_{RP} C_e^{g}}$	K_{RP}, b_{RP},g are the Redlich-Peterson constants

The values of isotherm constants were calculated using non–linear regression analysis and the results are listed in Table 2. The R values for all the isotherm models were beyond 0.90 indicating that all the models are fitting for explaining the adsorption mechanism of fluoride onto Cell-g-MAA/Carbon black. But the low value of Δq_e (%) and high values of R^2 for the Freundlich isotherm, indicating a very good mathematically fit of the Freundlich isotherm model. Since the values of n >1, it also confirmed the favorability of Freundlich isotherm model. The isotherm plots (only the isotherm plot at temperature 303 K is shown in Fig 1, further confirmed that the experimental equilibrium isotherm data fitted well to the Freundlich model in these studied conditions [24]. It can attribute to the fact that, the adsorption mechanism followed a multilayer adsorption mechanism. It can be due to the presence of primary,

secondary and tertiary amines on the surface of the adsorbent material. Also on going through the whole isotherm models the adsorption capacity K_F value seemed to be decreasing with respect to increase in temperature. Based on this fact it can be stated that the adsorption process is an exothermic process [25].

Table 2

Isotherm values for two parameter models and three parameter models at the four different temperatures

Isotherms	Parameters	Temperatures in Kelvin			
		293	303	313	323
Langmuir	q_m (mg/g)	147.57	165.99	162.25	172.70
	b (L/mg)	0.54	0.54	0.51	0.36
	R^2	0.946	0.926	0.925	0.946
	Δq_e (%)	2.57	3.21	3.73	2.97
Freundlich	K_F (L/mg)	60.24	66.14	66.10	58.36
	1/n	0.32	0.28	0.27	0.32
	R^2	0.999	0.999	0.999	0.999
	Δq_e(%)	0.32	0.28	0.38	0.42
Tempkin	K_T (L/mg)	38.40	49.46	37.67	20.32
	b (J/mol)	126.09	120.76	122.35	132.16
	R^2	0.949	0.945	0.959	0.949
	Δq_e(%)	7.17	5.36	6.12	5.89
Sips	q_S (mg/g)	155.75	172.22	167.91	171.06
	K_S	0.080	0.012	0.007	0.002
	n_S	2.31	1.28	2.28	2.32
	R^2	0.999	0.999	0.999	0.999
	Δq_e(%)	0.73	0.84	1.10	0.94
Redlich-Peterson	K_{RP}	2.38×10^3	6.69×10^3	2.15×10^3	4.29×10^3
	b_{RP}	37.23	95.01	30.99	6.06
	g	0.76	0.73	0.74	0.74
	R^2	0.993	0.997	0.995	0.994
	Δq_e(%)	2.87	1.74	2.16	2.76

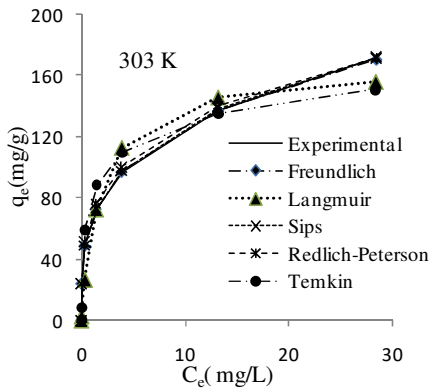

Fig. 5. Effect of isotherm models on MB adsorption for different concentrations

3.6. Thermodynamic Parameters

The thermodynamic parameters such as enthalpy and entropy of the adsorption process were determined from the slopes and intercepts of Van' Hoff plots using the following equations, $\Delta G^{0} = -RT \ln K_L$

(1)

$$\ln K_L = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT} \quad (2)$$

where ΔG^0 is the free energy change of specific adsorption (kJ/mol), R is the universal gas constant (J/K mol), T is the absolute temperature (K), K_L (L/g) is an equilibrium constant obtained by multiplying the Langmuir constants Q^0 and b, ΔS^0 (J/mol K) and ΔH^0 (kJ/mol) are the standard entropy and enthalpy changes of adsorption, respectively. The ΔG° values obtained were of negative values (-45.49, -46.25, -46.99 and -47.75 kJ/mol) for the four different temperatures (293,303,313 and 323 K). The negative values of ΔG° indicated that the adsorption process was a spontaneous process and at the same time it had explained the greatest affinity for fluoride onto the novel adsorbent Cell-g-MAA/Carbon black. Also it can be seen that the ΔG° values goes on increasing which was corresponding to a physisorption like mechanism [26]. The negative value of ΔH° (-23.41 kJ/mol) indicated an exothermic adsorption process and it implied that the adsorption process was energetically stable. The positive value of ΔS° (75.37 J/K mol) correspond to an increased degree of freedom (or randomness) of the adsorbed species. Based on all these factors it could be assumed that the MB adsorption process onto Cell-g-MAA/Carbon black was spontaneous and exothermic in nature.

CHAPTER 5

CONCLUSION

The present study was carried out to investigate the effectiveness of a novel adsorbent Cell-g-MAA in which carbon black being used as a filler. The adsorbent was used for the removal of methylene blue dye from aqueous solutions. From the experimental results and analysis, it can be concluded that adsorption is a simple, efficient, and economical method for dye removal, and the present adsorbent serves as a promising low-cost adsorbent.

The results clearly indicate that the adsorption of methylene blue onto Cell-g-MAA /Carbon black is highly effective under suitable conditions. The percentage removal of dye was found to increase with an increase in contact time, showing that adsorption is initially rapid due to the availability of a large number of active sites on the adsorbent surface. As time progresses, the rate of adsorption slows down and eventually reaches equilibrium, indicating that most of the active sites become occupied by dye molecules.

The study of initial dye concentration revealed that while the adsorption capacity increases with increasing concentration, the percentage removal may decrease at higher concentrations due to saturation of available adsorption sites. This highlights the importance of optimizing the concentration of dye for efficient removal.

Similarly, the effect of adsorbent dosage showed that increasing the amount of carbon black enhances the removal efficiency, as more surface area and active sites become available for adsorption. However, beyond a certain limit, the increase in adsorption becomes less significant, indicating the attainment of equilibrium conditions.

The pH of the solution was found to play a crucial role in the adsorption process. Since methylene blue is a cationic dye, adsorption is more favorable at higher pH values where the surface of carbon black becomes negatively charged, leading to stronger electrostatic attraction between the adsorbent and dye molecules.

The best fitted isotherm model was Freundlich, which implies a multilayer adsorption mechanism. Thermodynamic studies revealed an exothermic and spontaneous adsorption process.

Overall, the experimental findings confirm that Cell-g-MAA/Carbon Black has a good adsorption capacity for methylene blue and can be effectively used for the treatment of dye-contaminated wastewater. The material is inexpensive, easily available, and requires simple processing, making it suitable for practical applications, especially in developing regions.

In conclusion, this study demonstrates that Cell-g-MAA/Carbon Black is a viable and efficient adsorbent for dye removal, contributing to environmentally friendly and sustainable wastewater treatment solutions. Further research can be carried out to improve adsorption efficiency through surface modification and to apply this method on a larger industrial scale.

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