

Adsorption of Methylene Blue onto Surgical Mask-based Magnetic Activated Carbon

Thesis Submitted

By

Vikash Kumar

Roll No.-002010402025

Registration No.- 153981 of 2020-21

MASTER OF ENGINEERING

Under the supervision of

Prof. Ankush Majumdar

and

Prof. Somnath Mukherjee

JADAVPUR UNIVERSITY

FACULTY OF ENGINEERING & TECHNOLOGY

DEPARTMENT OF CIVIL ENGINEERING

(ENVIRONMENTAL ENGINEERING DIVISION)

KOLKATA-700032,

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Declaration

The Thesis titled “Adsorption of Methylene Blue onto Surgical mask-based Magnetic activated carbon” is prepared and submitted for the award of the degree of Master of Engineering in Civil Engineering course of Jadavpur University for the session of 2020-2022. I declare that the work described in this thesis is entirely my own. No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or institute. Any help or source information which has been awarded in the thesis, has been duly acknowledged.

Vikash Kumar

Vikash Kumar

M.C.E- 2ND Yr.

Roll No- 002010402025

Registration No.-153981 of 2020-21

Department of Civil Engineering

Environmental Engineering Division

Date 17/8/22

JADAVPUR UNIVERSITY
DEPARTMENT OF CIVIL ENGINEERING
KOLKATA-700132

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Signature of the supervisor and
date with office seal



Prof. Somnath Mukherjee

Department of Civil Engineering

Jadavpur University

Professor
CIVIL ENGINEERING DEPARTMENT
JADAVPUR UNIVERSITY
KOLKATA-32



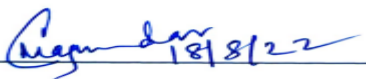
Prof. Ankush Majumdar

Department of Civil Engineering

Jadavpur University

Assistant Professor
Department of Civil Engineering
Jadavpur University
Kolkata-700 032

countersigned by



Dean

Faculty of Engineering and Technology

Jadavpur University



DEAN
Faculty of Engineering & Technology
JADAVPUR UNIVERSITY
KOLKATA-700 032



Head of the Department

Civil Engineering Department

Jadavpur University

Head
Department of Civil Engineering
Jadavpur University
Kolkata-700 032

JADAVPUR UNIVERSITY
DEPARTMENT OF CIVIL ENGINEERING
KOLKATA-700132

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Vikash Kumar

Vikash Kumar

M.C.E- 2ND Yr.

Roll No- 002010402025

Registration No.-153981 of 2020-21

Department of Civil Engineering

Environmental Engineering Division

Place: Kolkata

Date: 17/8/22

EXECUTIVE SUMMARY

For the preparation of activated carbon from surgical mask, ferric chloride was used as an activator. Experiments were conducted to determine the batch adsorption isotherms and kinetics of methylene blue (MB) on magnetic activated carbon (MAC). The Langmuir and Freundlich models were used to analyse experimental equilibrium data. The results show that the Langmuir isotherm equation provided the best fit, with a maximum MB adsorption capacity of 38 mg/g. The kinetic data obtained at various initial MB concentrations were analysed using pseudo-first order, pseudo-second order, and intraparticle diffusion models. The pseudo-second order model accurately described the adsorption kinetic data.

Graphical abstract

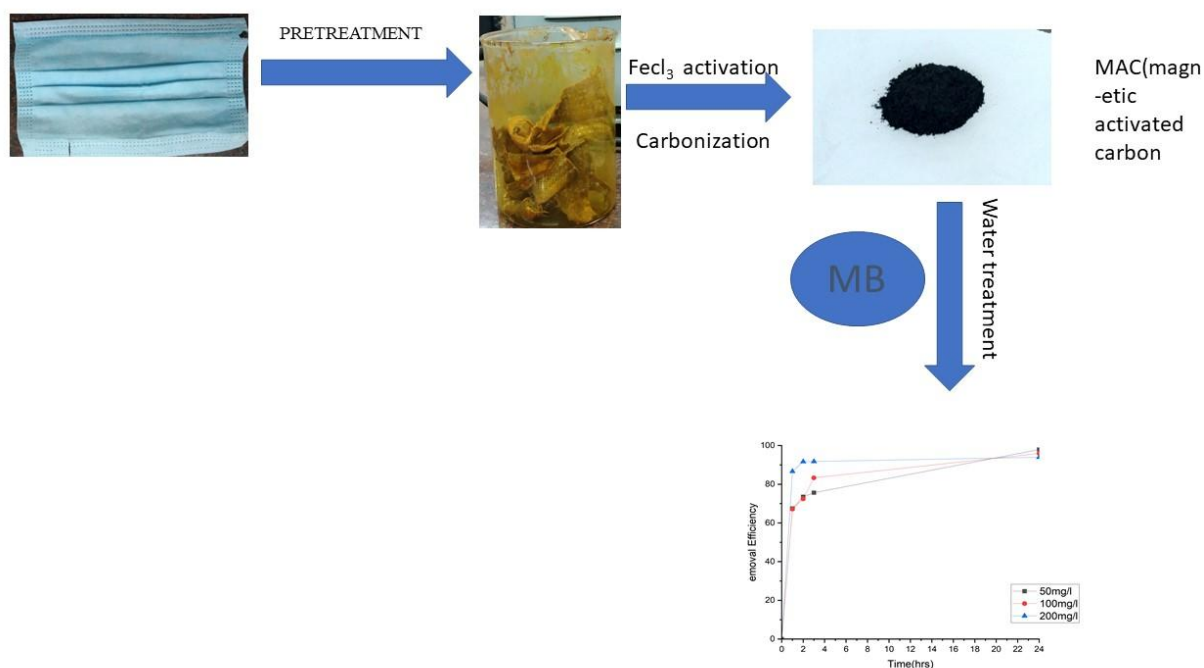


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LIST OF ABBREVEATIONS

ACF	Activated carbon fibre
AC	Activated carbon
GAC	Granular Activated carbon
MAC	Magnetic Activated carbon
MB	Methylene Blue
MPs	Microplastics
PAC	Powdered Activated carbon
PAN	polyacrylonitrile fibres
PPE	personal protective equipment

CHAPTER 1

Introduction

Excessive release of inorganic/organic pollutants into water as a result of industrialization, agricultural operations, and urbanisation has created a major environmental problem around the world. Many industries such as textile, leather, paper, plastics, tannery, cosmetics, rubber and paint use dyes to colour their products, which are some of the sources that generate dye bearing effluents (Ravikumar et al., 2005). Dye discharge into the environment is a problem for both toxicological and aesthetic reasons, as dyes obstruct light penetration, reduce the quality of receiving streams, are hazardous to creatures in the food chain, and sometimes carcinogenic (Padmesh et al., 2006). In addition, the dyes have a tendency to sequester metals and could be microtoxic to fish and other creatures (Afroze et al., 2016).

A cationic dye called methylene blue (MB) is frequently used for colouring as well as in microbiology, surgery, and diagnostics (Milani et al., 1992). MB can have some unwanted effects even though it is not particularly harmful. Acute MB exposure in people can lead to a higher heart rate, shock, the development of Heinz bodies, cyanosis, jaundice, quadriplegia, and tissue necrosis (Guo et al., 2018). MB creates eye burns that could permanently harm both human and animal eyes (Agarwal et al., 2016). As a result of the harmful effects on receiving waters, the treatment of effluents containing such dye is of interest. Dyes, in general, are poorly biodegradable or resistant to environmental conditions, and thus pose a major problem in the treatment of dye-containing wastewater. For the removal of dye contaminants from wastewater, a variety of technologies such as coagulation, foam flotation, precipitation, ozonation, ion exchange, filtration, solvent extraction, electrolysis, chemical oxidation, membrane technology, liquid–liquid extraction, and adsorption on activated carbon have been used (Bhatnagar & Minocha, 2006). Adsorption has been found to be an efficient and cost-effective method for removing dyes, pigments, and other colourants as well as controlling the biochemical oxygen demand (Cotoruelo et al., 2010). Commercial activated carbon has been used successfully to remove inorganics and organics from their aqueous phase. Commercial activated carbon, on the other hand, has limitations due to its high cost and regeneration issue. As a result, current research is focused on developing a more cost-effective and efficient adsorbent than activated carbon (Babaei et al., 2016). When compared

to other types of activated carbon, such as powder activated carbon and granular activated carbon, Activated carbon fibre is much more popular due to its ease of processing and rapid adsorption kinetics (Chiu & Ng, 2012). The major precursor materials for the preparation of activated carbon fibres (ACF) are viscose/rayon fibres, phenolic fibres, polyacrylonitrile fibres (PAN), asphalt fibres, and polyamide fibres, which have been used for commercial production for decades. Furthermore, natural fibre materials such as jute fibre, coconut fibre, and cotton (Chiu & Ng, 2012) were evaluated for their utilisation as raw materials because they are less expensive and renewable. Cotton, with its extremely high cellulose fibre content, low impurities (Chiu & Ng, 2012) and large production, could be a suitable replacement for viscose fibres in the preparation of ACF.(Duan et al., 2016).

SARS-CoV-2, a new type of coronavirus that is primarily transmitted through the respiratory route, recently caused the COVID-19 pandemic. In order to control the ubiquitous disease spread via the respiratory system, Experts recommend social or safe distancing measures (e.g. avoiding close personal contact) and, where this is not possible, PPE (personal protective equipment) (e.g., mask, glove, protective clothing gown, etc.) is a widely accepted method of self-protection. (Chiu & Ng, 2012)

Due to a lack of information, PPE will most likely be discarded without safety measures alongside other organic waste in regular municipal solid waste or, even worse, will be discarded directly in the environment. Discarded disposable gloves and masks have been discovered littering public places (e.g., parks and streets) all over the world (Chiu & Ng, 2012). This is due to the difficulty in achieving a reliable disposal scheme, given the heterogeneous composition of PPE and the risk of contamination, assuming disposable face masks and gloves were used in areas of high contamination risk (e.g., medical centres, public transportation, and centres). Because of the COVID-19 epidemic, waste management systems are under additional stress, which has led to the use of inefficient waste management techniques such local burning and direct dumps. However, even 1% of unregulated face mask production amounts to 10 million pieces, weighing between 30 and 40 tonnes. Moreover, plastic associated with COVID-19 has been discovered in marine ecosystems, pointing to a fresh source of oceanic microplastics (MPs). (Jung and others, 2021).

Surgical face masks, in particular, are made of a variety of polymers, including polyester, polypropylene, polyethylene, polycarbonate, polyacrylonitrile, and others, which are also used as raw materials in the production of other plastic products (Anastopoulos & Pashalidis,

2021). As a result, discarded single-use face masks, which may slowly degrade into smaller particles (< 5 mm) under ambient conditions, may become a new source of microplastics, causing environmental pollution and endangering living organisms.(Fadare & Okoffo, 2020)

Microplastics, in general, are not only a major environmental health concern hazard found in many marine habitats and biota(Ajith et al., 2020), but they also have an impact on humans crop production and food safety, as well as acting as carriers of major chemical pollutants in environmental systems that affect living organisms and, as a result, food safety(Ajith et al., 2020). According to recent research MPs potential role as hydrophobic organic chemical carriers (HOCs)(Ajith et al., 2020), antibiotics (Ajith et al., 2020), and heavy metals(Calero et al., 2019). In this context, studies related to the interaction of organic pollutants, including dyes, and other toxic substances (e.g. toxic metals, radionuclides etc.) is of fundamental importance to understand and describe the role of masks and mask-derived microplastics as pollutant carriers in environmental compartments (e.g. hydrosphere, biosphere etc.), and perform related environmental impact assessments.

MB dye adsorption which is aspect of this study have been presented here. The adsorption characteristics vary quantitatively and qualitatively with the nature of activated carbon, its processing and its origin. Hence, it is necessary to understand the kinetics and mechanism of adsorption under various process conditions. On the adsorption effectiveness of MB dye, the impact of operational variables including solution pH, sorbent dose, initial MB dye concentration, temperature, contact time, and their optimal values was examined. The Langmuir and Freundlich models were used to analyse the data from the adsorption equilibrium. A single-stage batch adsorbent has been used for the removal of MB dye in order to obtain information on the dynamics of the process.

CHAPTER 2

Literature Review

2.1 Types of Dyes

Dyes are the coloured organic compounds, it is generally used in solution to impart colour to various substances like fabric, paper, leather, hair, drugs, cosmetics, plastics and food material. It's a substance with a suitable colour and the ability to fix itself or be fixed to the fabric. It needs to be quick and resistant to water, dilute acids, alkalis, and a variety of organic solvents. The classification of dyes can be made with the view of three aspects which are (i) source of material (ii) chemical structure of dyes (iii) methods of application.

On the basis of source of material the dyes are classified in two categories which are natural dyes and synthetic dyes. Natural dyes are obtained from natural sources like plants (including fungi and lichens), animals, invertebrates or minerals. Examples of natural dyes are Indigo dyes (from stems and leaves of indigo), Alizarin dyes (from roots of madder plant), Logwoods dyes (from the trunk for black color to silk and cotton fabrics) etc. These dyes are not that much harmful in nature if present in environment. Synthetic dyes are prepared in labs/factories used for dyeing. The example of synthetic dyes are mordant dyes, azo dyes etc. Majority of dyes used today are synthetic because they are easy to use, cheaper, brighter, fast, have wider range of colors. These synthetic dyes are toxic in nature if present in water source which cause several health hazards for human beings.

A dye molecule has two main components based on its chemical structure: chromophores and auxochromes. Color is determined by the chromophore, while auxochromes aid in fibre attachment. On the basis of chromophores & auxochrome the dyes are nitro & nitroso dye, azo dye, triarylmethane dye, anthraquinone dye, Indigo dyes etc. In nitro and nitroso dye contain nitro group ($-\text{NO}_2$) and nitroso group ($-\text{NO}$) as the chromophores respectively and hydroxyl group ($-\text{OH}$) as auxochrome. One of the examples of nitro dye is Naphthol yellow S and nitroso dye is Gambine-Y. In azo dyes Azo group ($-\text{N}=\text{N}-$) is present as primary chromophore in their molecular structure which is present between two aromatic rings. Tartrazine (yellow), Methyl Orange, Congo Red, Bismarck Brown, Chrysoidine, and other azo dyes are examples. Azo dyes account for 60-70% of dyes used in food and textile

production. A central carbon is bonded to three aromatic rings in triarylmethane dyes, one of which is quinoid. The examples of triarylmethane dyes are Malachite Green (used as a direct dye for wool and silk), Crystal violet, and Phenolphthalein etc. In Anthraquinone dye Anthraquinone ring is the chromophore and -OH, -SO₃H, -NH₂ as auxochrome. One of the examples of this dye is Alizarin-red textile dye. In Indigo dyes have carbonyl chromospheres and indigoid structure (-CO=C=C-CO-). These dyes are used in cotton yarn, which is primarily used to make blue jeans denim cloth.

On the basis of methods of application the dyes are classified as Acidic dyes, Direct dyes, Vat dyes, Mordant dyes, Azoic dyes, Disperse dye, Sulphur dye, Basic dyes or cationic dyes, Reactive dye etc. Acid dyes are sodium salts of sulphonc and carboxylic acids. Acid dyes are anionic dyes that are water soluble. Nylon, wool, silk, and modified acrylics are all treated with it. Paper, leather, inkjet printing, food, and cosmetics all use them. Methyl Orange (MO) is an example of an acid dye. A neutral or slightly alkaline dye solution can be used to apply direct dye. Auxochromes that are acidic or basic are present. It has a polar nature and a strong affinity for cellulosic fibre. Martius yellow is an example of a direct dye. Insoluble in water, vat dyes are reduced in an alkaline bath and applied to cellulosic fibres as soluble leuco salts. In the fiber, the leuco forms are re-oxidized to the insoluble keto forms. Examples of vat dyes are anthraquinone and indigoid etc. Mordant dyes are used with the help of salts. Mordants – Al or Cr oxides salts (Sodium or Potassium dichromate mordant is added in the dye bath) are most suitable for wool and nylon. One of the examples of Mordant dyes is Alizarin. In azoic dyes two soluble components usually phenol or naphthol or aniline are impregnated in the fiber to form an insoluble color molecule. The examples of these type of dyes are Aniline phenyl azo, Para Red etc. Disperse dyes are insoluble in water and it is applied to hydrophobic fibers from an aqueous dispersion. It can form a colloidal dispersion in water. Crystal structure of fabric absorbs the colloidal particles. These dyes are used for synthetic fibers viz. polyester, nylon, cellulose acetate and acrylic fibres. The example of disperse dye is Duranol Red 2B. Sulphur dyes are used primarily for cotton and rayon, offers good wet fastness and variety of colours. It is not applicable for wool or silk. The example of sulphur dye is Indigo vat blue. Basic dyes, also known as cationic dyes, are water-soluble and appear in solution as colored cations. Applied to paper, polyacrylonitrile, modified nylons and modified polyester. The examples of these dyes are Chrysoidine, Methylene Blue. In reactive dye chromophore group that reacts with the substrate, forms a covalent bond with the fiber

usually cotton, wool and nylon. Examples of reactive dyes are Azophthalocyanine, formazan and anthraquinone etc.

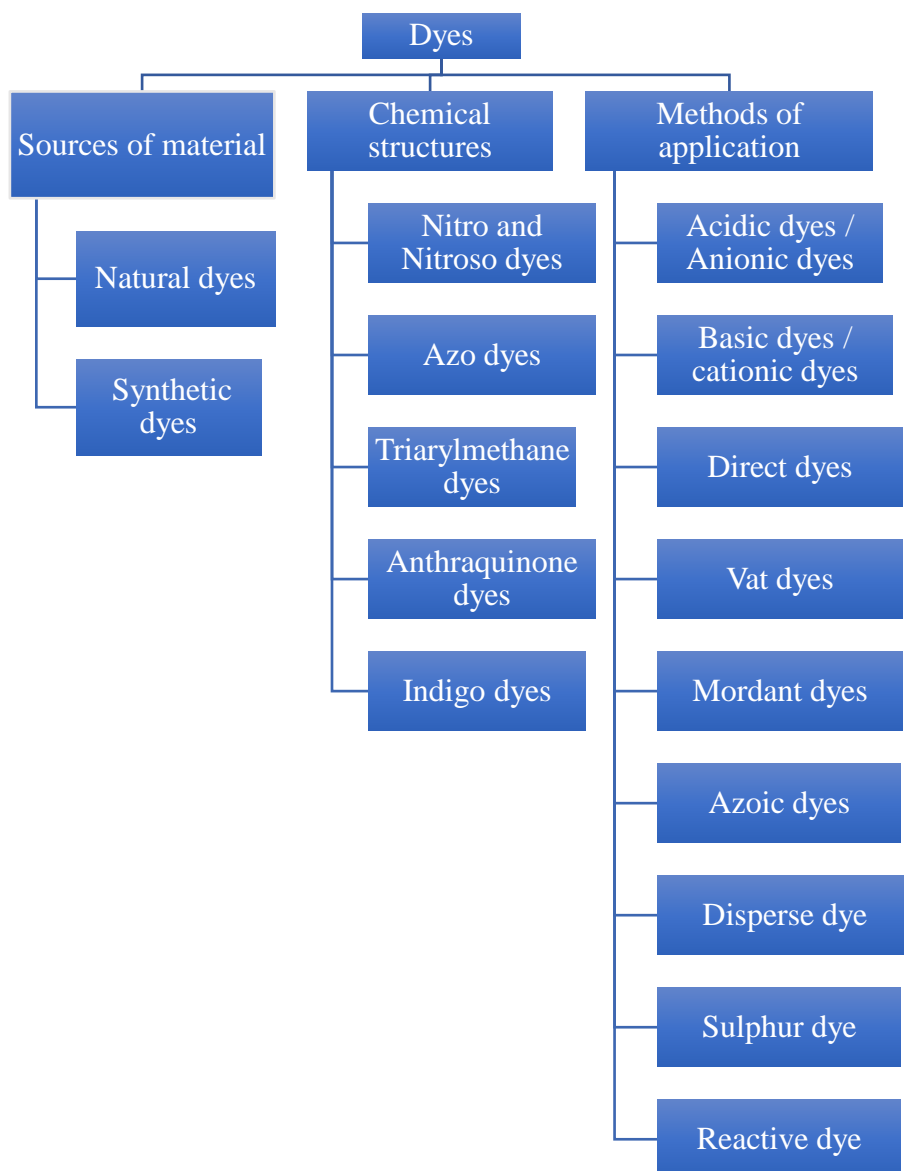


FIGURE 1: Classification of dyes

Dyes are mainly used in textile industries so textile industry effluent contains various types of color. Apart from that paint producing industry, paper industry, food processing industry also uses dye to impart color. So this industry also emits colourous wastewater.



FIGURE 2: Dye containing effluent from textile industries

2.1.1 Harmful effects of methylene blue dye

A typical cationic dye used for colouring as well as in microbiology, surgery, and diagnostics is methylene blue (MB) (Milani et al., 1992). Although it is not particularly harmful, it might have some unfavourable effects. Acute MB exposure in people can cause cyanosis, jaundice, quadriplegia, shock, tissue necrosis, and Heinz body formation (Guo et al., 2018). Eye burns brought on by MB have the potential to permanently harm both human and animal eyes (Agarwal et al., 2016). The treatment of effluents containing such dye is of importance due to the negative effects on receiving waters. Dye-containing wastewater treatment is extremely difficult because dyes, in general, are not biodegradable or environmentally friendly.

2.2 Defining the adsorbents types and listing empirical results

2.2.1 Type A adsorbents (activated carbon)

By carbonising and activating biomass, activated carbon (AC), a highly porous carbonaceous substance, is produced. It can be physically activated by steam or CO₂ or chemically activated by acids, alkalis, and salts. Typically, chemical activation is used to impregnate the reagents in either wet or dry circumstances. Because it takes less processing heat and time, chemical activation is preferable to physical activation. The high specific surface area of AC (often greater than 700m²/g) is its defining feature. Because adsorption is a surface phenomenon, AC's large surface area makes it suitable for the application. Commercial AC is available in powdered (PAC) or granulated (GAC) form (Popa & Visa, 2017), with both forms being used in adsorption applications. Commercial AC is typically expensive, so researchers are now investigating low-cost alternative feedstock for AC production (Hevira et al., 2021). The properties of the AC developed are also influenced by the nature of these low-cost alternatives. The performance of Activated carbon for the uptake of MB used is summarised in Table 1.

Table 1: Adsorption performance of MB by Type A adsorbent.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determinatio n	Highest RE(%)	q _{max} (mg/g)	Reference
AC from waste paper	7.0	25	1987	Langmuir	99.7	1657	(Tang et al., 2021)
AC from spent coffee ground	11	30	704.2	Sips	99.6	986.8	(C. Zhang et al., 2019)

AC from fox nutshell	–	30.0	2869	Langmuir	99.9	968.7	(Kumar & Jena, 2016)
AC from sorghum	6.6	55.0	1430	Langmuir	100	934.6	(H. Wang et al., 2018)
AC from Almond shell	8.8	–	2054	Langmuir	100	833.3	(Ait Ahsaine et al., 2018)
AC from sycamore	7.0	30.0	2434	Dubinin-Radushkevich	98.4	644.0	(Ma et al., 2019)
AC from Arundo donax		45.0	1784	Langmuir	99.8	480.8	(Üner, 2019)
AC from Persea species	10	20.0		Langmuir	98.0	365.6	(Regti et al., 2017)
AC from paper	7.0	20.0	1670	Langmuir	99.9	350.0	(Novais et al., 2018)
AC from Banana trunk waste	–	25.0	1173	Langmuir	99.9	227.3	(Hevira et al., 2021)
AC from charcoal	8.0	23.0	366.8	Langmuir-Hinshelwood	99.8	200.0	(Popa & Visa, 2017)
AC from chitosan	11	50.0	318.4	Langmuir	99.5	143.5	(Marrakchi et al., 2017)

2.2.2 Type B adsorbents (biosorbents)

Biosorbents are a type of adsorbent derived from biomass and other bio-materials that do not go through any thermochemical breakdown before use. Biosorbents are distinguished by the fact that they retain the original composition of the source bio-material. In the case of biomass, the constituents begin to degrade at temperatures above 300°C. Any biomass

material that has been processed at a lower temperature can still be used as a biosorbent. Plant parts include the leaves(Narvekar et al., 2018), bark, husk, peels(Lim et al., 2017), flower spikes, seeds, leaves, stem(Anfar et al., 2017), and living or dead microorganism cells. Wool fibres, egg shells, and baker's yeast are examples of biosorbents derived from animals. Though biosorbents do not have a large surface area, the abundance of different functional groups on the material allows for MB uptake via a variety of physicochemical interaction mechanisms. The performance of biosorbents for the uptake of MB used is summarised in Table 2.

Table 2: Adsorption performance of MB by type B adsorbents.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determinatio n	Highest RE(%)	q _{max} (mg/ g)	Reference
Glycerol based carbon	7.0	25	21.00	Langmuir	100	1050	(Narvekar et al., 2018)
Aegle Marmelos leaves	–	30	110.2	Langmuir	99.7	500.0	(Baruah et al., 2017)
Elaeisqueensis leaves	6.0	53	2.590	Langmuir	88.7	500.0	(Setiabudi et al., 2016)
Artocarpuscamansi peel	–	25	1519	Langmuir	90.0	409.1	(Lim et al., 2017)
Agro-food organic waste	10	25	471.9	Langmuir	100	285.0	(Anfar et al., 2017)
Maize silk powder	–	25	0.002	Langmuir	93.5	234.1	(Mirabouta

							lebi et al., 2017)
Tea waste	—	35	0.913	Langmuir	98.0	113.1	(L. Liu et al., 2018)
Lathyrus sativus husk	5.0	30	38.64	Langmuir	98.9	113.2	(I. Ghosh et al., 2021)
Terminalia catappa shell	5.0	25	69.88	Langmuir	90.6	88.62	(Hevira et al., 2021)
Oil tea shell	6.5	25	0.778	Langmuir	84.0	85.70	(J. Liu et al., 2016)
Sugarcane bagasse		25	829.0	Langmuir	24.0	76.00	(Giusto et al., 2017)
palm sawdust	8.0	25	43.40	Langmuir	96.0	53.94	(Esmaeili & Foroutan, 2019)

2.2.3 Type C adsorbents (biochar)

Biochar is a byproduct of biomass thermochemical processing methods such as pyrolysis, air gasification, steam gasification, and retort carbonization. Biochar is not the same as AC. Typically, these thermochemical processes are carried out with a greater emphasis on the fluid products (liquid and gaseous species), so the char produced is regarded as a residue. Though biochar is a pyrogenic carbon-rich material like AC, it lacks the latter's high specific surface area and distinct pore properties. The char is referred to as "biochar" because the

feedstock for the processes is biomass. However, the char produced by hydrothermal carbonisation is known as 'hydrochar.' The biodegradability of biochar as an adsorbent is a significant advantage. The performance of biochar for the uptake of MB used is summarised in Table 3.

Table 3: Adsorption performance of MB by Type C adsorbents.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determination	Highest RE(%)	q _{max} (mg/g)	Reference
Carbonised bamboo leaves + citric acid	7.5	32.0	393.3	Langmuir	99.9	725.0	(S. K. Ghosh & Bandyopadhyay, 2017)
Biochar from <i>Camellia oleifera</i> seed shell	–	25.0	1882	Langmuir	94.0	541.4	(Guo et al., 2018)
Modified biochar from <i>Eichhornia crassipes</i> (Water hyacinth)	10	30.0	57.08	–	99.5	395.0	(Yan Xu et al., 2016)
<i>Lacospermum secundiflorum</i> hydrochar	7.0	30.0	1135	Langmuir	96.0	359.0	(M. A. Islam et al., 2017)
Biochar from bamboo	5.0	25.0	298.6	Langmuir	80.0	184.1	(B. Wang et al., 2019)
Biochar from <i>Eucalyptus sheathiana</i> bark	11.3	35.0	73.00	Langmuir	90.0	104.2	(Dawood et al., 2016)
Biochar from Oak wood	7.0	50.0	245.7	Langmuir	98.2	97.55	(Babaei et al., 2016)
Biochar from reed	8.0	25.0	37.50	Sips	–	37.18	(Y. Wang et al., 2018)
Biochar from municipal waste	6.5	30.0	–	–	99.9	33.30	(Sumalinog et al., 2018)
Graphene-like carbon from sugar	8.0	–	674.6		99.5	20.00	(Lingamdinne et al., 2018)

2.2.4 Type D adsorbents (clays and minerals)

Clays and their minerals are naturally occurring earth materials with small particle sizes and a porous, layered structure with a large surface area. This allows for strong physical and chemical interactions with dissolved species in aqueous media, such as MB. Clay is classified into five types: kaolinite, montmorillonite, illite, bentonite, and chlorite. Clays can be modified in a variety of ways to improve their adsorption capacity for pollutants, the most common of which is the addition of surfactants. Metals can also be impregnated into the clay matrix to modify it. The performance of clays and minerals for the uptake of MB used is summarised in Table 4.

Table 4: Adsorption performance of MB by TypeD adsorbents.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determinatio n	Highest RE(%)	q _{max} (mg/g)	Reference
Natural clay	–	50.0	76.97	Langmuir	98.2	322.6	(Cool & Vansant, 2007)
Iraqi red kaolin clay	8.0	30.0	35.60	Langmuir	99.8	240.4	(Jawad & Abdulhameed, 2020)
Modified diatomaceous earth	8.0	25.0	195.0	Dubinin- Radushkevich	99.2	164.3	(Mohamed et al., 2019)
Birnessite	9.0	40.0	211.3	Langmuir	99.1	113.0	(Pang et al., 2017)
Kaolin + HCl + NaOH	11.2	18.5	45.00	–	100	111.0	(Boukhemkhem & Rida, 2017)

Na ₂ SiO ₃ ·5H ₂ O/Fe ₂ (SO ₄) ₃	9.0	—	334.4	Freundlich	80.5	53.79	(Abdelrahman et al., 2019)
Kaolin	6.0	25.0	21.27	Langmuir	98.0	52.76	(Mouni et al., 2018)
Fly ash-based Geopolymer	9.0	—	19.73	Freundlich	68.8	36.51	(El Alouani et al., 2018)

2.1.5 Type E adsorbents (polymers and resins)

They can come from Polymers are compounds composed of long, repeated chains of a single chemical unit (known as a monomer) either natural or synthetic sources. Polymers can achieve a wide range of chemical and physical properties due to their ease of manipulation via chemical modification. Each type of polymeric adsorbent has advantages and disadvantages. Biopolymers, such as chitosan and cyclodextrin, are easily degraded at high temperatures and, as a result, are unsuitable for use in packed columns. Polymeric adsorbents have the distinct advantage of being easily tuneable to achieve selectivity/affinity for specific pollutant species via a variety of chemical modification techniques. The main limitation is the price. It is more expensive to synthesise than other adsorbent classes. Furthermore, inorganic/synthetic polymeric adsorbents are not biodegradable and can harm the environment if not fully recovered before effluent release.

Table 5: Adsorption performance of MB by Type E adsorbents

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determination	Highest RE(%)	q _{max} (mg/g)	Reference
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Calcium alginate	6.9	15.0	—	Langmuir	84.6	3506	(Q. Li et al., 2017)
Starch-based hydrogel	9.0	35.0	—	Langmuir	95.2	2967	(L. Chen et al., 2021)
Modified calcium alginate	6.0	25.0	13.56	Langmuir	97.3	2358	(Q. Wang et al., 2019)
Calcium alginate	5.0	25.0	—	Langmuir	78.0	1282	(B. Wang et al., 2019)
Alginate	—	22.0	—	Langmuir	75.5	1144	(B. Wang et al., 2018)
Waste tyre rubber	10	—	—	—	99.0	834.0	(M. T. Islam et al., 2018)
Modified Chitin sorbent	—	—	—	—	79.8	568.0	(Cao et al., 2018)
Poly (Acrylonitrile-co-Acrylic acid), Thiourea	9.0	25.0	26.31	Langmuir	—	308.6	(Shean et al., 2019)
Sulphonic groups functionalised Mxenes	2.0	85.0	—	Langmuir	59.9	221.2	(Lei et al., 2019)
Macrogel polyvinyl alcohol	6.0	25.0	613.8	Langmuir	94.2	181.8	(Shoueir et al., 2016)
Polydopamine microspheres	—	25.0	13.00	Langmuir	98.4	161.3	(Fu et al., 2016)
Polyvinyl alcohol	6.0	—	—	Langmuir	61.3	123.3	(Agarwal et al., 2016)

Polyaniline	–	28.0	–	Langmuir	96.0	19.67	(Maruthapandi et al., 2018)
Polyzwitterionic resins	5.0	25.0	–	Langmuir	80.0	14.90	(Saleh et al., 2017)
Zeolite from Kaolin of Dehessa, Egypt	7.0	25.0	364.2	Langmuir	79.5	13.49	(El-Mekkawi et al., 2016)
Polypyrrole-coated cotton textile	7.0	25.0	–	Langmuir	96.0	6.830	(Ayad et al., 2018)
Zeolite/HCl	7.0	25.0	21.40	Langmuir	98.8	2.113	(Hor et al., 2016)

2.1.6 Type F adsorbents (nanoparticles)

Nanoparticles are a type of material with sizes ranging from 1 to 100nm. They have a large surface area due to their small size. Because adsorption is a surface phenomenon, materials with large surface areas will always be preferred as good adsorbents. Chemical vapour deposition, precipitation, sol-gel, hydrothermal synthesis, and other techniques can be used to generate nanoparticles from organic and inorganic sources. Chemical reactions in the gaseous phase in the vicinity of a heated surface produce nanoparticles for chemical vapour deposition. Precipitation is the most widely used synthesis method because nanoparticles are formed as precipitates from solutions.

Table 6: Adsorption performance of MB by Type F adsorbents.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determination	Highest RE(%)	q _{max} (mg/g)	Reference
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Graphene Oxide	11.5	–	–	Langmuir	98.6	2273	(Peng et al., 2016)
Modified graphene	5	45	–	Langmuir	86.5	1429	(Sham & Notley, 2018)
Modified MnO	9	25	38.70	Langmuir	99.8	154.0	(Yuelong Xu et al., 2019)
Modified Nanodiamond	–	25	–	–	86	47.62	(Esmaeili & Foroutan, 2019)
Nano-clay Magadiite	6	50	39.00	–	98.6	20.00	(Hevira et al., 2021)
Charcoal	8	23	251.8	Langmuir	53	100.0	(Popa & Visa, 2017)

2.1.7 Type G adsorbents (composites adsorbent)

Recently, scientists have started investigating how to mix various adsorbent classes to optimise performance, increase affinity for particular adsorbates, or for other reasons. The term "composite adsorbents" refers to them. A composite material is made up of two or more components that are physically and/or chemically unrelated and have been mixed to create special qualities or characteristics for a given purpose. As a result, these adsorbents were assigned a separate class in the analysis because their properties differed from those of their parent constituents. For MB adsorption, a wide range of composite adsorbents have been developed, with compositions spanning all adsorbent classes.

Table 7: Adsorption performance of MB by Type G adsorbents.

Adsorbent name	pH	Temp(°c)	SSA (m ² /g)	Method of q _{max} determination	Highest RE(%)	q _{max} (mg/g)	Reference
Magnetic alginate/ MWCNTs	–	25	–	Langmuir	99.5	905.5	(Boukhalfa et al., 2019)
Biochar from banana peel/ FeSO ₄	6	40	–	Langmuir	–	862.0	(P. Zhang et al., 2020)
Graphene oxide/MgO	11	–	–	Langmuir	–	333.0	(Fajarwati et al., 2019)
Magnetic alginate/Rice husk	–	–	–	Langmuir	89	344.0	(Alver et al., 2020)
Fe ₂ O ₃ /MOF	8.9	40	197.8	Langmuir	94.6	325.6	(Yan Xu et al., 2016)
Fe ₃ O ₄ NPs/Sodium alginate/AC	8	25	183.6	Langmuir	89.5	465.1	(C. Li et al., 2017)
Fe ₃ O ₄ /Montmorillonite	7.3	20	147.9	Langmuir	99.5	106.4	(Chang et al., 2016)
Fe ₂ O ₃ NPs/Biochar from paper sludge	12	–	15.30	Langmuir	99.0	50.00	(Yan Xu et al., 2016)
Fe ₃ O ₄ /Chitosan	12	–	–	Langmuir	80.6	20.41	(Foroughi et al., 2020)

2.3 Critical review of literatures

Photodegradation, electro-coagulation, ozonation, membrane processes, and biological processes have all been widely used for MB removal from water environment. Adsorption is reported to be immensely effective for dye remediation in concerning pollutant generating industries owing to handle pollutants at low concentrations, cost-effective, relatively easy regeneration, and less chemical residues leave behind. The major limitation of activated carbon is high chemical cost as a result of which researchers are now investigating low-cost alternative feedstock for AC production. Though the available Bio sorbents do not have a large surface area, the abundance of various functional groups on the material allows for MB uptake via a variety of physicochemical interaction mechanisms more efficiently. However, each type of polymeric adsorbent has advantages and disadvantages. Biopolymers, such as chitosan and cyclodextrin, are easily denatured at high process temperatures and fragile in nature for which, are unsuitable for use in packed bed reactor columns. Furthermore, inorganic or synthetic polymeric adsorbents are not biodegradable and can harm the environment if not fully recovered before effluent release causing secondary pollution. The main disadvantage of using nanoparticles is their ecotoxicity when they are not properly recovered from solution and released into the environment. The use of activated carbon may have been compelled by its perceived suitability for adsorption. Adsorption is a surface phenomenon, so materials with a large surface area are always preferred. Due to unnatural condition of the country use of surgical mask have been telescopically increased in the society and all the parts of the world. But proper disposal methodologies of surgical mask after usages not clearly unveil in the literature. But no such extensive work has been addressed in the published document to use the waste material as adsorbent though due to presence of polymeric surface it is apprehended the same may be a useful material for MB removal. The kinetics equilibrium capacity is required to be examined.

CHAPTER 3

Objective and Scope of work

3.1 Objective

The objective of the present study is to prepare market available surgical mask derived activated carbon for effective and feasible removal of methylene blue (MB) dye from water environment.

3.2 Scope of work

Following scopes of the studies are broadly considered in the present investigation

- Synthesis of mask based adsorbing material both parent and Ferric chloride impregnated material.
- Characterization of novel Fe impregnated carbon material using XRD study.
- Determining pH_{zpc} to examine its ionic effect impression.
- Batch adsorption study for exploration of uptake potential of the abovementioned material with time – concentration studies and dosages time of contact etc
- Kinetics evaluation and various isotherm studies to examine adsorption mechanism.

CHAPTER 4

Materials and Methods

4.1 Preparation of Adsorbent

Material 1(M₁)

In this experiments Single-use surgical masks were used for the sorption experiments without any prior special treatment, except that the aluminium strip and the rubber straps were removed. The single used surgical mask was heated in the muffle furnace up to 400 °C for different time interval such as .5 hr, 1hr, 1.5hr, 2 hr. For time interval .5 hr ,1hr we got sticky type of material which we cannot use for adsorption. We have done adsorption experiment with material synthesised at 1.5hr & 2 hr.

Material 2(M₂)

Single-step method for the preparation for MAC(magnetic activated carbon)

The MAC was synthesised in one step of carbonization and activation. Surgical mask (10.0 g) with small particles was mixed with 50 mL of FeCl₃ aqueous solution (the mass ratio of FeCl₃ to surgical mask was 2: 1, 20 g of FeCl₃&6H₂O was dissolved in 50 mL of distilled water and FeCl₃ aqueous solution was obtained) and kept at room temperature for 24 hours. The samples were then dried before being placed in an aluminium crucible and heated for 60 minutes in a muffle furnace at 700°C. The carbonised, activated materials were then washed with HCl aqueous solution, deionized water until the pH of the washing solution reached 6–7, filtered, and finally dried at 110 °C for 24 hours. The MAC was obtained and stored in tightly closed bottles.

4.2 Adsorbate and other chemicals

MB, the typical basic cationic dye, was selected as the adsorbate in this study. The formula of MB dye is C₁₆H₁₈N₃SCl.3H₂O with a molecular weight of 319.86 g/mol was supplied by MG Enterprises. A stock solution of 1,000 ppm MB was prepared by dissolving the appropriate amount (1,000 mg) of MB in a litre of distilled water. The working solutions were prepared by diluting the stock solution with distilled water to give the appropriate concentration of the

working solutions. The pH of the solutions was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions, respectively. All sample bottles and glassware were cleaned and then rinsed with deionized water and oven-dried at 60°C. The VISIBLE-SPECTRO 105 spectrophotometer was used to determine the concentrations of MB dye in solution. The concentration of the residual dye was measured using visible spectrometer at a λ_{max} corresponding to the maximum adsorption for the dye solution ($\lambda_{\text{max}} = 665 \text{ nm}$) by withdrawing samples at fixed time intervals and centrifuged, and the supernatant was analysed for residual MB. Calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance–concentration profile.

4.3 Adsorption experiments

Batch adsorption studies involved varying the initial dye concentration, and dosage of the adsorbent at predetermined time intervals. These batch adsorption studies were conducted using a methodology that has already been published (Afroze et al., 2016). The mixture was shaken in a constant temperature Orbital Shaker Incubator at a speed of 120 rpm and a temperature of 30°C. At a specified time, bottles from shaker were taken out. The dye concentration was determined using the linear equation of the calibration curve, and the absorbance of the supernatant was measured at the wavelength that corresponded to the sample's maximum absorbance. At time t , the amount of dye adsorbed onto the surgical mask, q_t (mg/g) and percent adsorption were calculated from the linear equation of the calibration curve. The amount of dye adsorbed onto surgical mask at time t , q_t and % adsorption is calculated from Eqs. (2) and (3), respectively:

$$q_t = \frac{(c_0 - c_t)V}{M} \dots\dots\dots(1)$$

and dye removal efficiency, that is % of adsorption, was calculated as:

$$\% \text{ adsorption} = \frac{c_0 - c_t}{c_0} \times 100 \dots\dots\dots(2)$$

where C_0 is the initial dye concentration (milligrams per litre), C_t is the concentration of dye at any time t (min), V is the volume of dye solution (l), and m is the mass of surgical mask powder (g).

4.4 Kinetics experiments

There are mainly three steps involve during the adsorption of adsorbate to the surface of the adsorbent. In the first step, molecular mass transfer from the solution to the adsorbent surface occurs. Then, internal molecular diffusion to the adsorption sites placed on the adsorbent takes place. The adsorption is then completed in the final step of the process. The investigation of adsorption kinetics is very important to estimate the adsorption mechanism. For this purpose, the adsorption kinetics models such as the pseudo-first-order, the pseudo-second-order, and intraparticle diffusion models are widely applied to the adsorption systems.

Adsorption kinetics were evaluated and analysed using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, as stated below, in order to examine the mechanism of adsorption and the transient behaviour of the dye adsorption process.

Pseudo-first-order and pseudo-second-order kinetic models.

Lagergren created the pseudo-first-order model. The linearized integral form of the pseudo-first-order is commonly written as(Nandi et al., 2009):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad \dots\dots\dots(3)$$

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and time, t (min), respectively. K_1 is the pseudo-first-order adsorption equilibrium rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ vs. time, t , provides K_1 , and q_e can be calculated

Similarly, the linearized form of the pseudo-second-order kinetic model (Ahmad et al., 2014) is shown in below equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots\dots\dots(4)$$

where K_2 is the pseudo-second-order adsorption equilibrium rate constant [g/(mg min)]. A plot of t/q_t vs. t can be used to calculate the rate constant K_2 (g/mg min), initial sorption rate h (mg/g-min), and q_e (mg/g).

The constant K_2 is used to calculate the initial sorption rate h , at $t \rightarrow 0$, as follows:

$$h = k_2 q_e^2 \quad \dots\dots\dots (5)$$

Using Eq(4), we can calculate the rate constant K_2 , initial adsorption rate h , and predicted q_e from the plot of t/q_t vs. time t .

Intra-particles diffusion model.

For design purposes, the intra-particle diffusion model is used to identify the adsorption mechanism (Yan Xu et al., 2016). The amount of adsorption varies almost proportionally with $t^{0.5}$ rather than with contact time in most adsorption processes.

$$q_t = k_{id} t^{0.5} + I \quad \dots\dots\dots (6)$$

where q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of time. K_{id} is the intra-particle diffusion rate constant (mg/gmin^{0.5}), which can be calculated from the slope of the linear equation of the plot q_t versus $t^{0.5}$. I (mg/g) is a constant that represents the thickness of the boundary layer.

4.5 Isotherm experiments

Equilibrium adsorption studies were conducted by contacting 50 ml of dye solutions of different initial concentration of 20, 50, 100, 200 with 5 mg of surgical mask powder in a series of 10-ml vial for a period of 24 hrs which was more than sufficient to achieve equilibrium time.

The adsorption isotherm of any adsorption system is defined as a curve of the amount of adsorbed molecules to the adsorbent surface as a function of the adsorbate's partial pressure or concentration at a constant temperature.

4.5.1 Langmuir isotherm

Irving Langmuir (Gases, 1918) proposed the Langmuir adsorption model, and the main assumptions of this isotherm model are as follows.

- Adsorption occurs at specific binding sites that are localised on the surface of the adsorbent.
- All adsorption sites on the surface of the adsorbent are identical.
- The surface of the adsorbent is covered with a monolayer of adsorbed molecules.
- There is no interaction between the adsorbed molecules on the adsorbent surface.

The following equation illustrates the Langmuir adsorption model:

$$\frac{c_e}{q_m} = \frac{1}{k_l q_{max}} + \frac{c_e}{q_{max}}$$

C_e (mg /l) and q_m (mg/g) are the equilibrium concentration of the molecules and the amount of adsorbed molecules on the surface of the adsorbent at any moment respectively, in the equation above. The maximal adsorption capacity (mg/g) is represented by q_{max} , while the Langmuir constant (L/ mg) is represented by K_L .

4.5.2 Freundlich isotherm

This is approach for describing multilayer and heterogeneous adsorption of molecules to the adsorbent surface is the Freundlich isotherm model (Freundlich, 1899). Equation illustrates this model is.

$$\log q_m = \log k_f + \frac{1}{n} \log c_e$$

where q_m (mg/g) is the amount of molecules adsorbed to the adsorbent surface at any given time, C_e (mg/l) is the equilibrium concentration, and n and K_F are the Freundlich constant and Freundlich exponent, respectively. K_F (mg/g) denotes the adsorbent's adsorption capacity toward the adsorbate, and n denotes the degree of surface heterogeneity and describes the distribution of adsorbed molecules on the adsorbent surface. A value of n greater than 1 indicates favourable adsorption of the molecules onto the adsorbent surface. A higher n value indicates greater adsorption intensity.

Results and Discussion

5.1 Adsorption study of MB with material M_1

In this experiment material M_1 was used for removal of MB from aqueous solution. The removal efficiency of MB for different concentration are shown in Figure3. From the plot it appears that maximum removal efficiency was 81.7% for initial concentration of MB was 20 mg/l. As we increase the initial concentration the removal efficiency is significantly decreases from 81.7% to 67.63% for initial concentration range of 20 and 100mg/l. It has very low adsorption capacity of 3.26mg/g for 81.7% of efficiency. It indicates that this material has very low adsorption capacity for MB.

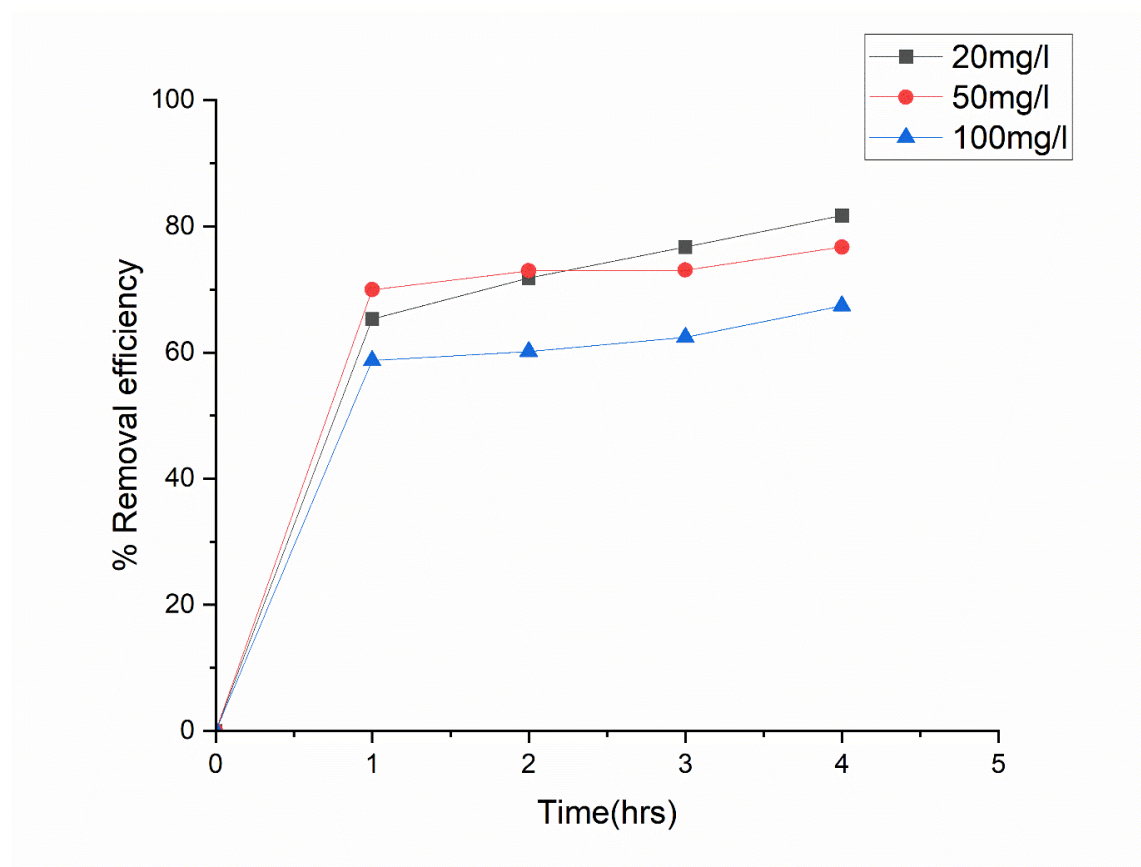


Figure3: % Removal of MB by M_1 .

[Adsorbent dosage: 0.05g; V: 10 mL; pH: (Unadjusted); Rotational speed: 120 strokes/min; T: 303 K.]

5.2 Characterization of MAC

5.2.1 Determination of the pH of zero point of charge (pH_{ZPC}) for MAC.

The pH of zero point of charge (pH_{ZPC}) is the pH value at which the solid's surface is considered neutral. It is important during the sorption of ionic species from aqueous systems on solid surfaces. The pH_{ZPC} plots for MAC is shown in Figure 4.

The results indicate that the surface of MAC is close to neutrality ($\text{pH}_{\text{ZPC}} = 6.9$). At pH values below pH_{ZPC} , the MAC surface is positively charged, whereas at pH values above pH_{ZPC} , the MAC surface is negatively charged. Surface protonation occurs at lower pH values (pH 2 and 3) due to the frequent interaction and accumulation of H^+ ions from the bulk, which have the tendency to surround the surface of the adsorbent. Furthermore, the MAC surface is assumed to release basic OH^- ions into the bulk, resulting in a slight increase in the final pH of the suspension. As a result, at lower pH values, this results in an overall positively charged MAC surface (below pH_{ZPC}). However, at alkaline pH (or above MAC's pH_{ZPC}), the surface of MAC was discovered to be negatively charged.

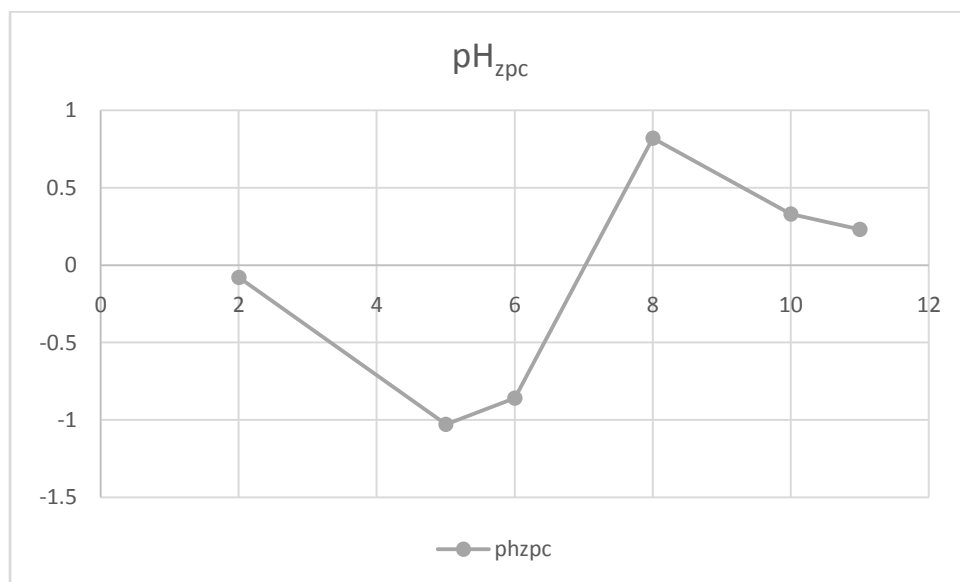


Figure 4: Determination of the pH of zero point of charge (pH_{ZPC}) for MAC.

5.2.2 XRD study of MAC

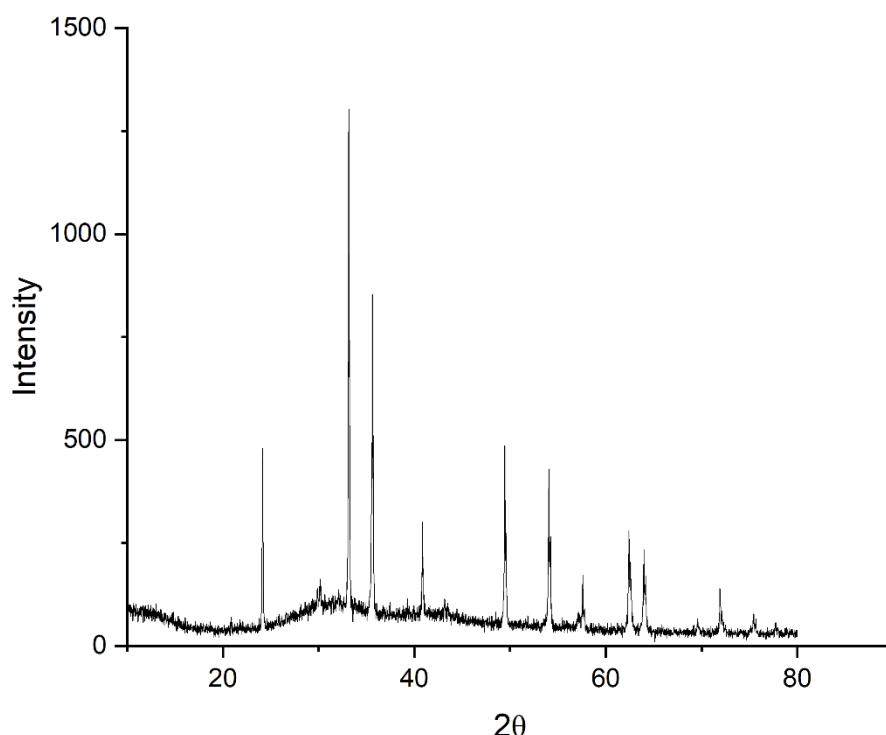


Figure 5: XRD spectrum of MAC

The XRD spectrum of the prepared MAC is shown in Figure 5. The peaks at 2θ -30.10°, 35.45°, 43.12°, 53.57°, 56.92°, and 62.56° on the XRD spectrum for MAC, are indexed as the planes of (475), (1312), (857), (542), (511) and (400) and are characteristic absorption peaks for magnetite (Fe_3O_4) according to PDF card 19-0629. (C. Chen et al., 2019). The XRD spectrum showed that the magnetic carbon was successfully synthesized and the magnetic material was Fe_3O_4 . The characteristic peaks for the activated carbon were not obvious, and this phenomenon could be due to the influence of Fe_3O_4 with a high absorption peak and a high crystallinity.

5.3 Adsorption study of MB with MAC (M_2)

Adsorption experiment focuses on the effects of parameters that have a significant impact on the adsorption process. Adsorbent dosage, initial dye concentration, and contact time are among the parameters.

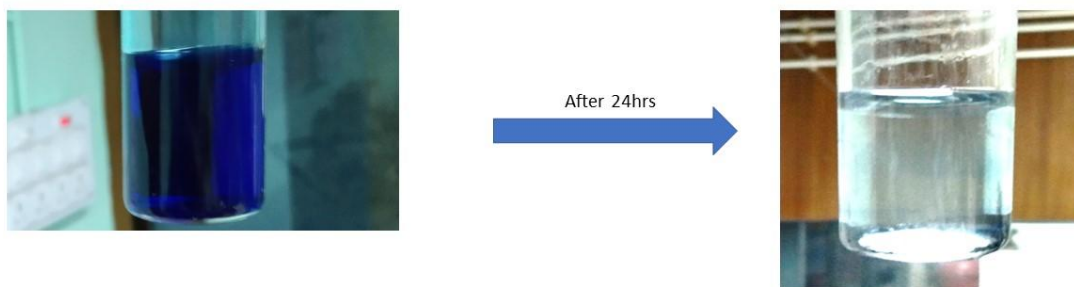


Figure 6: Photo image of 100 mg/L of MB solution before and after the adsorption experiment.

5.3.1 Effect of Adsorbent Dosage

The adsorbent dosage parameter studied in order to determine an adsorbent's capacity for a given concentration of dye in solution. Figure 7 shows the effect of surgical mask FeCl_3 activated carbon (MAC) dosage on the removal of MB. According to the graph, the percentage removal of MB increased as the MAC dosage increased. This is due to increased MAC surface area and the availability of more adsorption sites as a result of increased MAC dosage. The highest removal of MB by MAC in this study was 0.05 g with 97.94 percent removal. Extending the MAC dosage beyond 0.05 g resulted in no detectable changes.

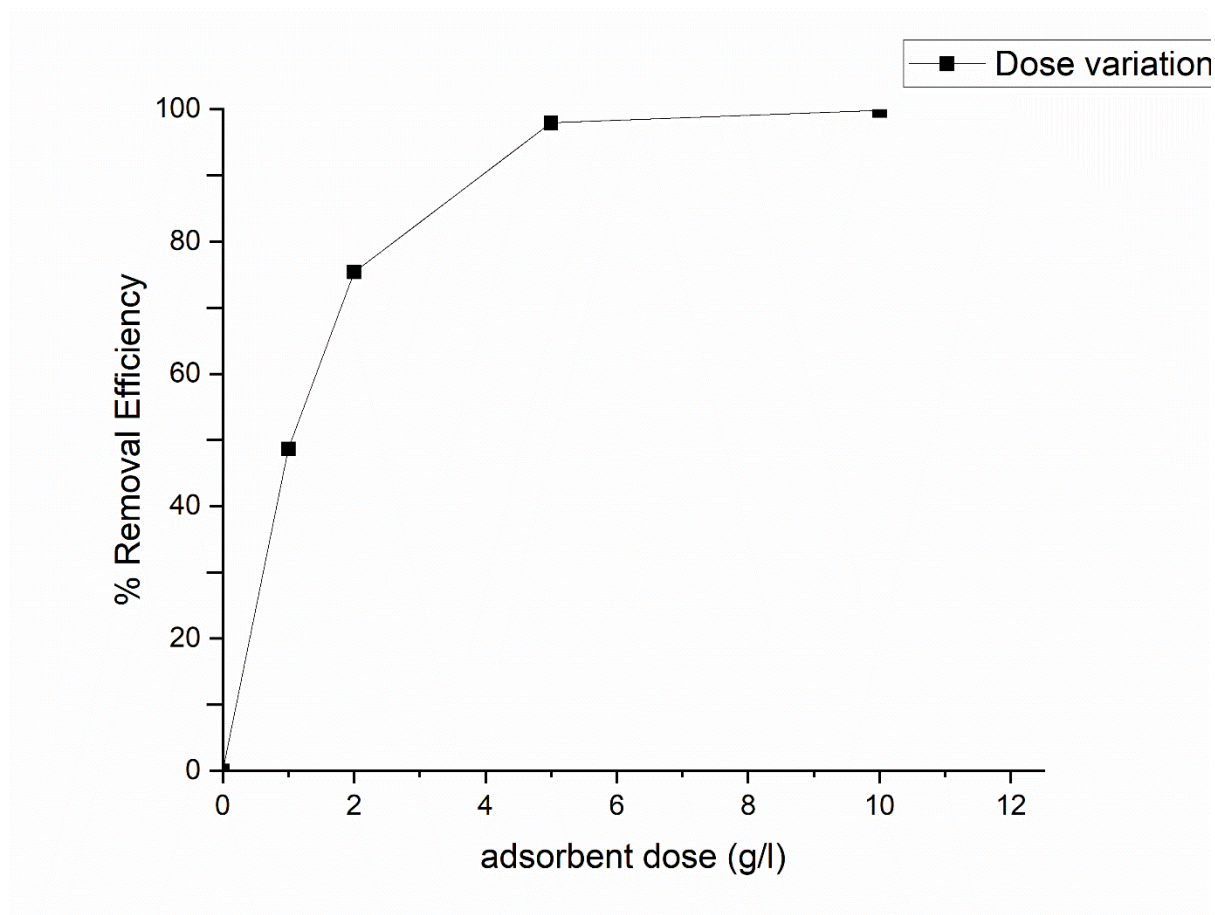


Figure7: Effect of MAC dosage on the MB removal

[MB concentration: 50 mg/L; V: 10 mL; pH: (Unadjusted); Time: 24 hrs; Rotational speed: 120 Rotation/min; T: 303 K]

5.3.2 Effect of Concentration and Contact Time

The direct correlation between the initial dye concentration and the available binding sites on the adsorbent's surface determines the impact of the initial dye concentration. This study examined the impact of adsorption capacity with an initial MB concentration range of 50 to 200 mg/L at 303 K. Figure 8 illustrates the MB adsorption capacities by MAC at various concentrations. With an increase in MB concentration from 50 to 200 mg/L, the amount of MB adsorbed increased rapidly from 9.79 to 37.58 mg/g. As MB concentrations increases, so the collision rate between MB cations and MAC is also increases. As a result, more MB cations were transferred to the surface of the MAC.

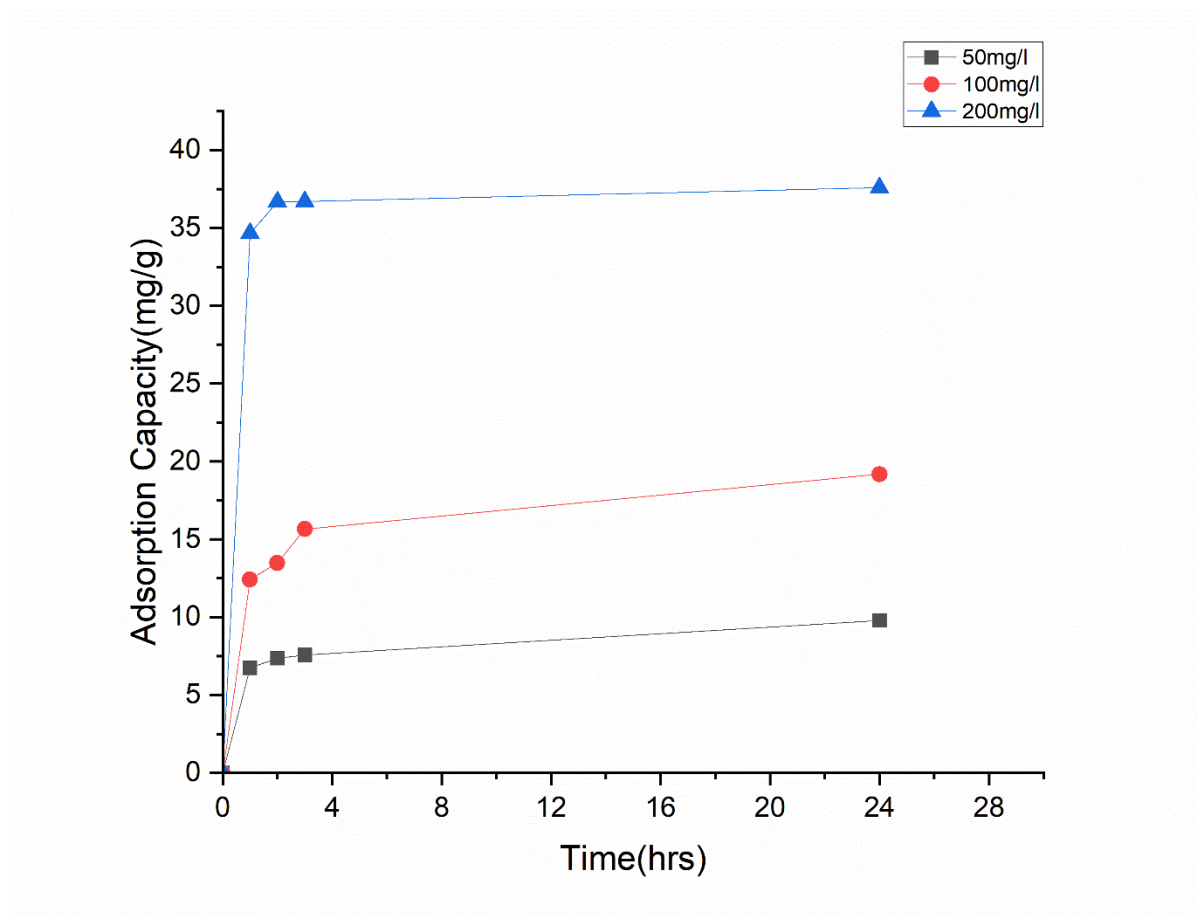


Figure8: Effect of MB concentration on the adsorption capacity of MB by MAC.

[Adsorbent dosage: 0.05g; V: 10 mL; pH: (Unadjusted); Rotational speed: 120 strokes/min; T: 303 K.]

5.3.3 Kinetic studies

Two kinetic models, Pseudo-First Order and Pseudo-Second Order were tested on experimental data to investigate the potential rate controlling step. The parameters used in these two kinetic models, as well as the regression coefficient R^2 , are summarised in Table 8, 9 and Figure 9(a,b). The parameters of the pseudo-second order dynamic model are found to be better than those of the pseudo first order dynamic model. The pseudo second-order kinetic equation model demonstrates that adsorption occurs in two stages, the first of which is fast and the second of which is slower. The first stage of the adsorption process begins with physical adsorption via van der waal interaction, in which the adsorbate approaches the adsorbent's surface to form an ionic or covalent bond, resulting in a chemical adsorption process in which the adsorbate adheres strongly to the adsorbent and is not easily desorbed. Most dye adsorption processes use the chemisorption process, which is influenced by the

chemical properties of the adsorbent material in the form of biomass (organic) to the dye. In addition, the adsorption capacity and predicted value obtained from the experiment are consistent. This is consistent with previous research (Tang et al., 2021). It can be said that adsorption occurs through surface adsorption and the functional groups on the MAC surface may involve in the adsorption of dye molecules.

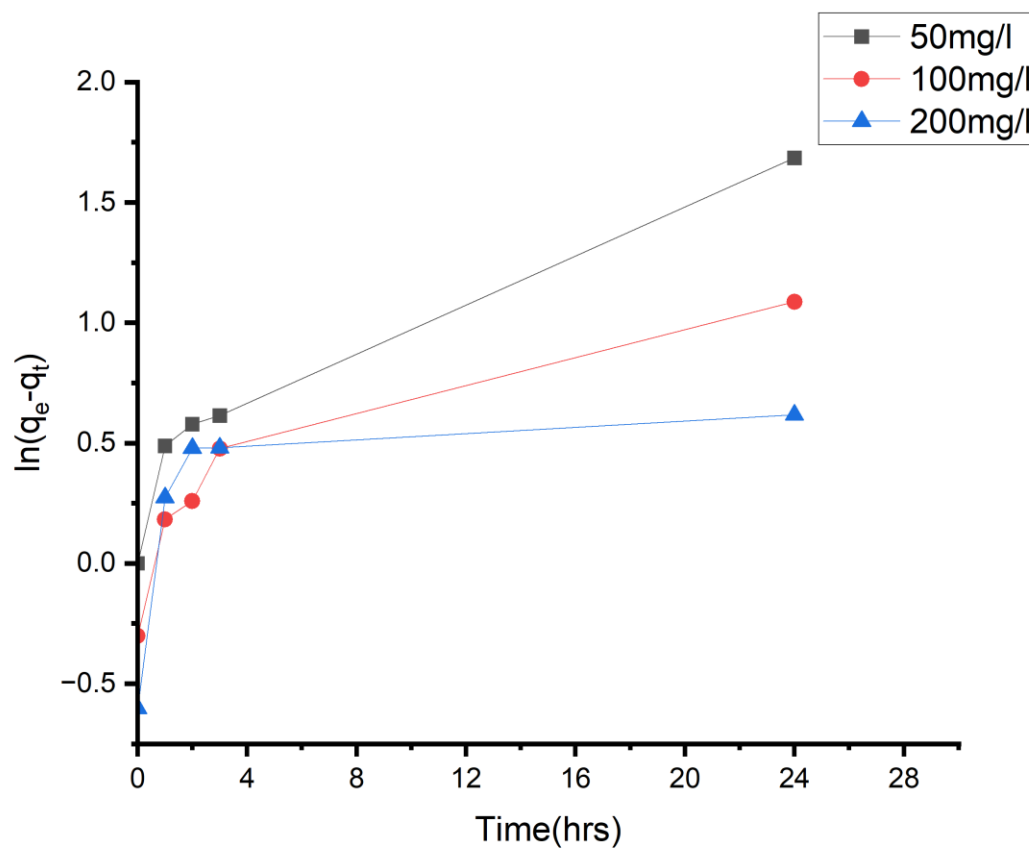


Figure 9(a): Pseudo first order dynamics

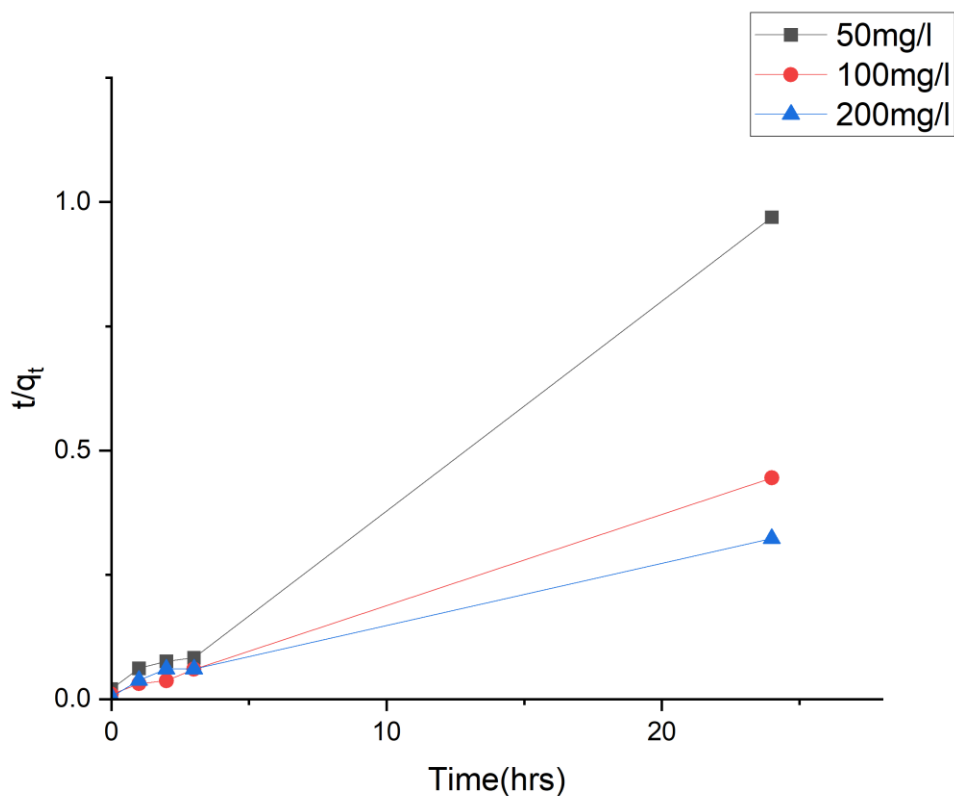


Figure 9(b): Psuedo Second order dynamics

TABLE 8:Pseudo-First Order adsorption parameter applied to experimental data for the adsorption of MB by MAC at 303 K

Concentration(mg/l)	Pseudo first order	
	K_1	R^2
50	0.05	0.9018
100	0.045	0.8076
200	0.034	0.75

TABLE 9:Pseudo-Second Order adsorption parameter applied to experimental data for the adsorption of MB by MAC at 303 K

Concentration(mg/l)	Pseudo Second order	
	K_2	R^2
50	0.041	0.9965
100	0.0096	0.9968
200	0.0085	0.991

5.3.4 Isotherm studies

Adsorption isotherms can be used to predict the interaction between the amount of adsorbate adsorbed by the adsorbent (q_e) and the amount of adsorbate remaining in the solution after the system has reached equilibrium (C_e). In this study, two isotherm models, namely Langmuir (1918) and Freundlich (1906) were employed. The parameters of the isotherm models were listed in Table 10. Based on the calculated data, the Langmuir model is found to be linear over whole concentrations ($R^2 \geq 0.99$), with adsorption occurring over a surface with homogeneous energy sites that are equally available for interaction. However, Langmuir model is found better suited in the present case.

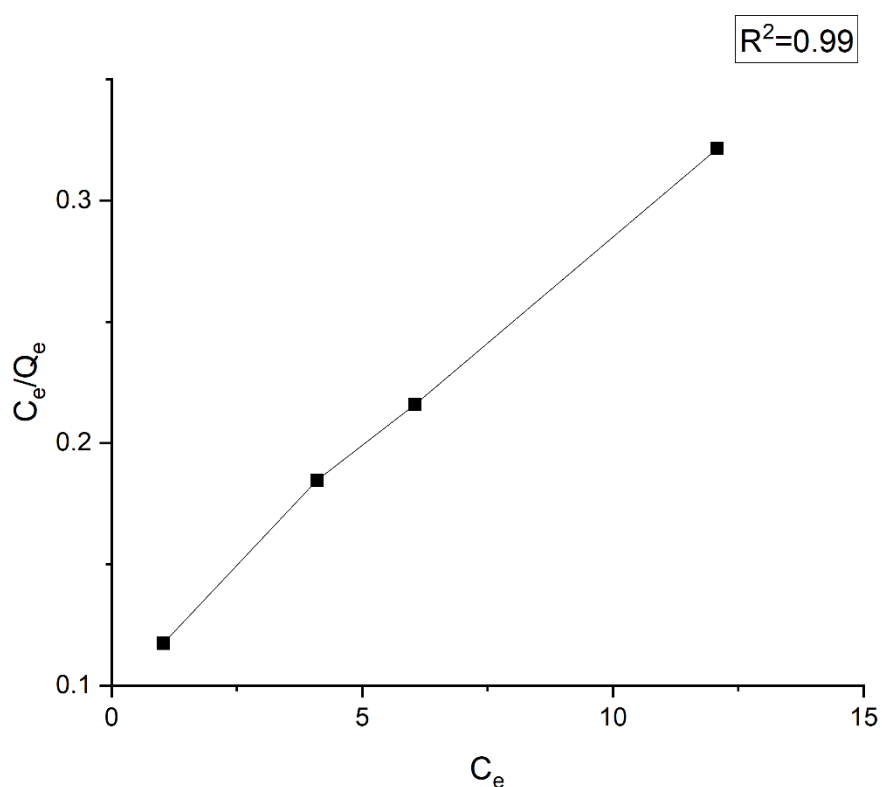


Figure10(a): Langmuir isotherm model

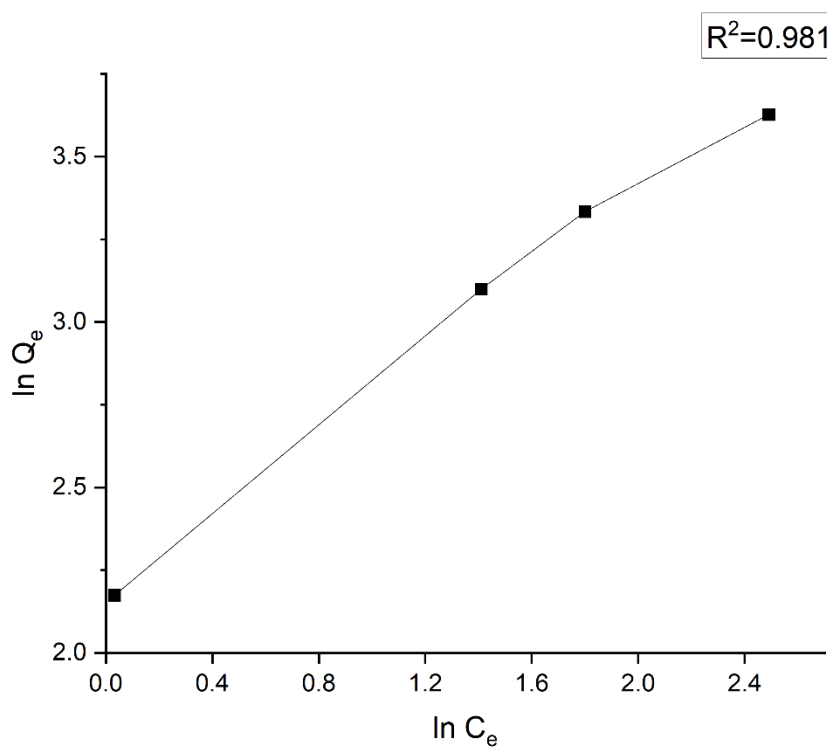


Figure10(b): Freundlich isotherm model

TABLE 10:Langmuir and Freundlich isotherm models parameters for MB adsorption onto MAC

Langmuir Isotherm

q_{\max} (mg/g)	k_L (L/mg)	R^2
37.58	0.03	0.99

Freundlich Isotherm

$1/n$	$k_F[(\text{mg/g}) (\text{L/mg})^{1/n}]$	R^2
0.104	48.9	0.981

5.4 Comparison of MAC with other adsorbents

Table 11: Comparison of adsorption capacity of the MB removal by different adsorbents

Source of AC	pH	Temp(°c)	Isotherm determination	RE(%)	q _{max} (mg /g)	Reference
steel slag	7.0	20	Langmuir	82	41.62	(Cheng et al., 2018)
sawdust	7.0	30	Langmuir	90	30.00	(Montoya-Suarez et al., 2016)
Coconut fibres	3.0		Langmuir	85	21.30	(L. Zhang et al., 2018)
Textile	6.2	30	Langmuir	89	17.83	(Wong et al., 2018)
waste tyre	3.0	25	Langmuir	90	1.050	(Daraei & Mittal, 2017)
Surgical Mask	7.7	30	Langmuir	98	38	Present study

Adsorption isotherms can be used to predict the interaction between the amount of adsorbate adsorbed by the adsorbent (q_e) and the amount of adsorbate remaining in the solution after the system has reached equilibrium (C_e) (Njoku et al. 2014). Freundlich (1906) and Langmuir (1918) isotherm models were used in this study. Table 10 shows the parameters of the isotherm models. Based on the calculated data, the Langmuir model is found to be linear over whole concentrations ($R^2 \geq 0.99$), and it is assumed that adsorption occurs at specific binding sites located on the adsorbent's surface. All adsorption sites on the adsorbent's surface are identical. A monolayer of adsorbed molecules covered the MAC's surface. It means that there is no interaction between the molecules that have been adsorbed on the adsorbent surface. Table 11 compares the monolayer adsorption capacity (q_{max}) for MAC with MB to that of other types of AC adsorbents.

Two kinetic models, Pseudo-First Order and Pseudo-Second Order, were tested on experimental data to investigate the potential rate controlling step. The kinetic parameters for MB adsorption by MAC are listed in Table 8,9. The R^2 values for the Pseudo-Second Order model are higher ($R^2 \geq 0.99$). As a result, the Pseudo-Second Order model fits the adsorption of MB by MAC better than the Pseudo-First Order model. The Pseudo-Second Order analysis of kinetic data revealed that the rate-controlling step is chemisorption, which involves

valence forces via electron exchange or sharing between adsorbate molecules and adsorbent surface functional groups.

The present work describes the use of ferric chloride as the surface modified activating agent in the preparation of carbons from surgical masks. The derived carbons obtained in this work exhibited high MB adsorption efficiency for cationic dyes. Table 11 exhibits the maximum adsorption capacity and removal efficiency of AC made from other biomass. The results show that compared to AC made from other biomass materials, such as steel slag, sawdust, coconut fibres, textile, and waste tyre, present synthesised AC has a higher adsorption capacity and removal efficiency. All these indicate that new method of preparation of MAC through surgical mask is better than other adsorbent. Presented adsorption capacities are in a superior range than those described in the bibliography for methylene blue.

Conclusion

A surgical mask-based MAC was successfully prepared using a single-step carbonization magnetization activation with FeCl_3 as follows: The FeCl_3 to surgical mask mass ratio was 2:1. 20.0 g of surgical mask was mixed with 50 mL of FeCl_3 aqueous solution was added and left for 24 hours, before being dried overnight and undergoing a one-step carbonated activation for 60 min at 700 °C. There were Fe–O groups on the MAC surface, and Fe_3O_4 existed in the pores and surfaces of the MAC. The adsorption process was chemisorption process, followed by the pseudo-second-order model. The prepared MAC was used to adsorb MB in an aqueous solution and it shows adsorption isotherm are well describe by Langmuir isotherm model and its maximum adsorption capacity was 38 mg/g. Surgical masks-based MAC was found to be effective for MB adsorption and is easily separated and recovered using an external magnetic field. MAC has the potential to be used as an adsorbent in the treatment of organic pollutant wastewater.

CHAPTER 7

Future scope of the study

A multi-component aqueous phase is commonly encountered in real adsorbent applications. These complexities are typically not captured by batch adsorption experiments (and thus the adsorption capacity values) used to synthesise standard MB solutions. Some adsorbate species may hamper MB adsorption and significantly reduce its adsorption capacities.

Packed columns can be used for adsorption in industrial applications. They are also used as the final stage of treatment for polluted water before it is released into the environment. Its ability to regenerate will suggest that it can be used effectively in these columns.

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