

**DEVELOPMENT OF MODIFIED MOF-5 TOWARDS ENHANCING
MALACHITE GREEN DYE REMOVAL FROM AQUEOUS SOLUTION**

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**DEVELOPMENT OF MODIFIED MOF-5 TOWARDS ENHANCING
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by

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LIST OF SYMBOLS

Symbol	Description	Unit
B_1	Heat of sorption	mg/L
C	Intraparticle diffusion kinetic model constant	mg/g
C_e	Equilibrium dye concentration	mg/L
C_o	Initial dye concentration	mg/L
k_1	Pseudo-first-order rate constant	min ⁻¹
k_2	Pseudo-second-order rate constant	min ⁻¹
k_{diff}	Intraparticle diffusion rate constant	mg/g·min ^{-1/2}
K_f	Adsorption capacity factor	-
K_L	Langmuir isotherm constant that related to the binding sites affinity and adsorption energy	L/mg
K_T	Equilibrium binding constant	-
m	Adsorbent mass	g
n	Adsorption intensity	-
q_e	Equilibrium amount of removed adsorbates per number of adsorbents used / Equilibrium adsorption capacity	mg/g
q_m	Maximum monolayer adsorption capacity	mg/g
Q_{max}	Maximum adsorption capacity of adsorbents	mg/g
q_t	Amount of removed adsorbate at time t	mg/g
R^2	Coefficient of determination	-
R_L	Separation factor / Equilibrium parameter	-
V	Dye solution volume	L

LIST OF ABBREVIATIONS

Symbol	Description
AC	Activated Carbon
AgOH-NP	Silver Nanoparticles
AOP	Advanced Oxidation Process
BDC	Benzenedicarboxylic Acid
BET	Brunauer-Emmett-Teller
BTC	Benzene-1,3,5-tricarboxylic acid
CFA	Coal Fly Ash
COD	Chemical Oxygen Demand
CP	Coordination Polymer
DMF	N,N-Dimethylformamide
EDS	Energy-Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphite Oxide
Ind	Industry
MG	Malachite Green
Mil-53(Al)-NH ₂	Aluminium-based MOF
MMcf	Million Cubic Feet
MOF	Metal-Organic Framework
MSPE	Magnetic Solid-phase Extraction
MWCNT	Multi-wall Carbon Nanotubes
NPC	Nanoparticle
PAN	Polyacrylonitrile

POM@UiO-66	Polyoxometalate Encapsulated Zirconium-BDC MOF
RHA	Rice Husk Ash
SEM	Scanning Electron Microscope
UV	Ultraviolet
XRD	X-Ray Diffraction
ZIF	Zeolitic Imidazole Framework

**PEMBANGUNAN MOF-5 YANG DIUBAHSUAI UNTUK MENINGKATKAN
PENYINGKIRAN PENCELUP HIJAU MALAKIT DARI LARUTAN**

AKUEUS

ABSTRAK

Sintesis MOF-5 dan pengubahsuaianya telah disiasat untuk menyingkirkan pencelup hijau malakit. Bahan penjerap MOF-5 yang diubahsuai telah disintesis dengan menggunakan abu sekam padi (yang diperoleh dari pembakaran sekam padi pada suhu yang berbeza), dan/atau abu arang batu pada nisbah yang berbeza. Penjerap disediakan dan dicirikan melalui pembelauan sinar-X, spektroskopi transformasi inframerah Fourier, mikroskop imbasan elektron dengan penyebaran tenaga spektroskopi sinar-X, dan analisis Brunauer-Emmett-Teller. Melalui ujikaji primer, MOF-5/RHA&CFA/2:1 telah dipilih sebagai penjerap yang terbaik untuk penyingkiran pencelup hijau malakit dari larutan akueus. Terdapat beberapa faktor, seperti kepekatan awal pewarna, kadar goncangan, suhu, pH larutan, jumlah penjerap, dan masa penjerapan dianggap sebagai parameter operasi penting yang mesti dioptimumkan. Contohnya, kepekatan awal pencelup MG pada 150 mg/L, kadar goncangan pada 300 rpm, 40 °C, 11.5 untuk nilai pH larutan, 0.2 g/ 100 mL untuk jumlah penjerap per unit isipadu larutan, dan 4 jam masa penjerapan. Tambahan pula, kajian isoterma dan kinetik penjerapan menunjukkan bahawa model isoterma Langmuir dan kinetik pseudotertib kedua memberikan kelakuan pemodelan terbaik untuk penjerapan MG kepada penjerap yang berprestasi terbaik seperti yang dinyatakan di atas. Selain itu, analisis BET mendedahkan bahawa permukaan BET tidak mempunyai hubungan dengan kecekapan penjerapan pewarna MG.

DEVELOPMENT OF MODIFIED MOF-5 TOWARDS ENHANCING MALACHITE GREEN DYE REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

The synthesis of MOF-5 and its modification have been investigated for malachite green dye removal. The modified MOF-5 adsorbents have been prepared using rice husk ash (obtained from rice husk burning at various temperatures) and coal fly ash at different ratios. The adsorbents are prepared and characterised using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscope with energy dispersive X-ray spectroscopy, and Brunauer-Emmett-Teller analysis. From the preliminary test, the MOF-5/RHA&CFA/2:1 has been chosen as the best adsorbent for malachite green dye removal from the aqueous solutions. Several factors, like initial dye concentration, shaking rate, temperature, solution pH, amount of adsorbent, and contact time, were the important operating parameters that must be optimised. In this study, at 150 mg/L initial MG dye concentration, 300 rpm shaking rate, 40 °C, 11.5 for solution pH value, 0.2 g/100 mL of the adsorbent amount per solution volume, and 4 hours of contact time. Furthermore, adsorption isotherms and kinetics studies indicated that Langmuir isotherm and pseudo-second-order kinetic models provide the best modelling behaviours for MG adsorption onto the best-performed adsorbent. The BET analysis indicates that the BET surface area has no relationship with the MG dye adsorption efficiency.

CHAPTER 1

INTRODUCTION

This chapter provides an overview of this study and the significance of MOF-5 in the adsorption of Malachite Green (MG) dye. Generally, this chapter describes the research background of MG dye removal, problem statements, and research objectives of this study.

1.1 Research Background

Treating polluted wastewater is still a major challenge nowadays. The consumption of untreated wastewater could contribute to diarrhoeal diseases or even death as the world's population grows continuously. The demand for textiles and colouring stuff increases drastically because dyestuff has been widely utilised in various industrial sectors such as textiles, papers, cotton, wool, leather, plastic, pharmaceuticals, food, and cosmetic products (Sartape et al., 2017; Sajab et al., 2011). More than 10000 types of dye are produced annually, with an average production of 7×10^5 tonnes (Altintig et al., 2018). In 2020, the textiles industry led the dyes market in revenue, accounting for more than 62% of the market (Grand View Research, 2021).

The handmade textile industry, locally known as the batik industry, is highly recognised and has been highly commercialised, significantly contributing to the economic prosperity in Malaysia, particularly in the states such as Kelantan, Terengganu, and Sarawak. This industry has traditionally been passed down from generation to generation, especially in the Malays community. High-quality batiks demand high skills and proper equipment and materials (Ahmad et al., 2002). Due to the demand for colouring materials increasing exponentially, coloured waste discharge causes serious water pollution. Generally, dyes are highly stable and poorly biodegradable, which can stay in wastewater for a long time, even in critical conditions

(Sartape et al., 2017; Borousan et al., 2019). Coloured wastes interfere with sunlight penetration into the water, limiting aquatic photosynthesis (Chanzu et al., 2019). These compounds not only contain toxic chemicals to certain aquatic species but may also cause allergic reactions, dermatitis, skin irritation, and cancer in humans (Wang et al., 2014).

MG is one of the water-soluble cationic dyestuffs commonly used to paint silk, wool, leather, and paper (Altintig et al., 2018). It is also used in aquaculture as a fungicide and antiseptic to reduce fish parasites and diseases (Zhang et al., 2008). It is usually in the form of greenish powder and is classified under triphenylmethane (Raval et al., 2016c). The physicochemical properties of MG are shown in Table 1.1. MG is persistent in the environment and difficult to remove from aqueous solutions. It is very harmful to various aquatic and terrestrial creatures, including microbes. Both acute and chronic exposures are particularly deadly to freshwater fish. It causes major public health risks as well as potential environmental issues. So far, clinical and experimental findings indicate that MG is a kind of toxin in many human organs. For instance, it decreases the rate of growth, digestion and fertility; damages important organs such as the spleen, liver, kidney, and heart; causes skin, lung, eye, and bone diseases; and has teratogenic effects. Mammalian cells are extremely cytotoxic to it. After the rats were exposed to MG, tumours were found in the breast, lungs, and ovaries. After MG exposure, there was a decrease in red blood cell amount (dyscrasia), haemoglobin (anaemia), and haematocrit percent (Srivastav et al., 1997; Srivastava et al., 2004; Yonar and Yonar, 2010). Although this dye is prohibited from being used in certain countries and by the US Food and Drug Administration due to its carcinogenic and teratogenic effects, until now, many places still using it because of its abundance, cheapness, and efficacy, as well as the absence of a suitable substitute (Hameed and

El-Khaiary, 2008a; Papinutti et al., 2006). However, there is no specific law stating the prohibition of using MG in Malaysia. Furthermore, MG residues were detected in fish purchased from the Malaysian market (Kwan et al., 2018).

Metal-organic frameworks (MOFs) are a kind of porous polymeric material composed of metal ions linked together by organic bridging ligands that offer a novel development at the intersection of molecular coordination chemistry and materials science (James, 2003). They are grouped under a unique category of coordination polymers (CPs) where there are strong interactions between the metal-ligand which are stronger than hydrogen bond, as well as greater directionally than the other weak interactions, such as π - π bonding (Hu et al., 2018; Fan et al., 2018). Hoskin and Robson (1990) work on synthesising scaffolding-like structural 3D frameworks by combining tetrahedral or octahedral arrays of metal centres with organic moieties. Since MOF is flexible in that the geometry, size, and functionality can be varied, over 20000 distinct MOFs have been reported and examined in the past decade (Furukawa et al., 2013). Yaghi et al. (1995) were involved in inventing novel structures based on the assembly of metal ions arranged to organic moieties as linkers. The group successfully synthesised MOF-5 in 1999, indicating the start of the research into novel structures of different types of dimensional frameworks (Tranchemontagne et al., 2008).

Doubtless, MOFs with distinct structural and chemical properties have enormous potential in a wide range of applications, normally separations. Among the several MOFs identified, MOF-5 has been largely studied due to its apparent surface areas, which have become a promising material in various potential applications such as adsorption, gas storage, catalysis, and sensor application (Opelt et al., 2008). MOF-5 has the chemical formula $Zn_4O[C_6H_4(CO_2)_2]$ or can be written in $Zn_4O(BDC)_3$,

where BDC represents 1,4-benzodicarboxylate (Kaye et al., 2007). Figure 1.1 shows the cubic framework of MOF-5. Figure 1.2 visualises Zn_4O , the node, whereas Figure 1.3 visualises BDC, which is the struts (ChemTube3D, 2021). The MOF-5 has a cubic structure, an average pore diameter of 18.6 Å, and a massive pore size, nearly 20 Å, resulting in high sorption of gaseous hydrogen (McGaughey and Kaviani, 2004).

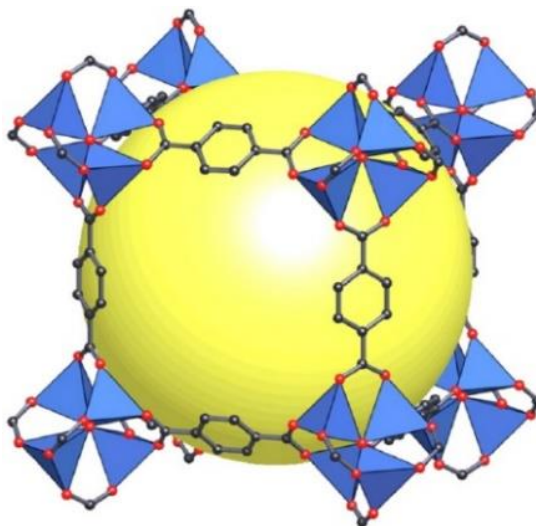


Figure 1.1 1-by-1-by MOF-5 3D Cubic Framework Model. (Yellow Sphere: Pore Volume) (Kaye et al., 2007).

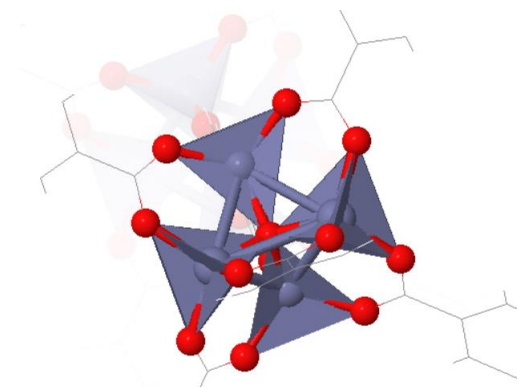


Figure 1.2 Zn_4O node (Blue-grey: Zinc, Red: Oxygen) (ChemTube3D, 2021).

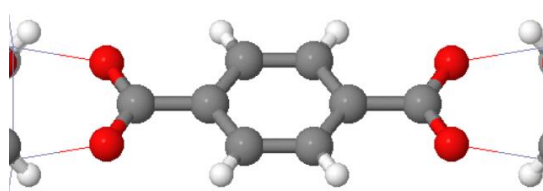
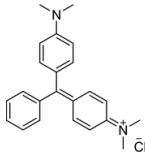
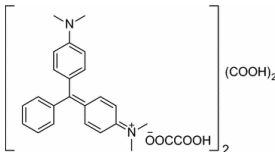


Figure 1.3 BDC strut. (Grey: Carbon, White: Hydrogen) (ChemTube3D, 2021).

Table 1.1 Physicochemical properties of MG dye (Raval et al., 2016b).

Parameters	Description	
Common name	Malachite green chloride	Malachite green oxalate
Molecular formula	$C_{23}H_{25}ClN_2$	$C_{52}H_{54}N_4O_{12}$
Molecular weight	364.9 g/mol	927.0 g/mol
IUPAC name	[4-[[4-(Dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium; chloride	[4-[[4-(Dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium;2-hydroxy-2-oxoacetate
Molecular structure		
Other names	Aniline green; Basic green 4; Diamond green B; Victoria green B	
Colour index number	42000	
CAS number	123333-61-9	
Maximum wavelength	618 nm	

1.2 Problem Statement

Based on the literature review, MG is still widely used worldwide, either in the dyestuff or aquaculture industries. Removing MG from wastewater is critical as it leads to serious health defects for aquatic organisms and humans. MOF-5 shows great potential in dye removal in terms of efficiency and capacity. However, pristine MOF-5 adsorbents are usually unstable and inefficient in adsorption capacity (Feng et al., 2012). Currently, improving the mechanical strength and thermal-, chemical-, and hydro-stability of MOFs while retaining high activity and the specific surface area remains a significant challenge in the actual applications, particularly in high-temperature and high-humidity environments (Wang and Serre, 2019; Wei et al., 2019; Wang et al., 2019). Thus, MOF-5 adsorbent modification is needed to enhance its capability. Silica can be added to stabilize the MOF-5 during the adsorption to achieve higher efficiency. The silica can come from solid waste from burning processes such as coal fly ash (CFA) and rice husk ash (RHA). Mostly, some power plants may dispose of CFA in surface impoundments or landfills. Under the plant's water discharge permit, others may discharge it into a nearby waterway (United States Environmental Protection Agency, 2014). RHA is treated and handled as waste and disposed of at landfill sites due to its difficulty in handling and transportation (Jongpradist et al., 2018). RHA and CFA are the abundant biomass and solid wastes to be dumped into landfills annually. Due to their high silica content, they can be reused as sustainable silica sources. However, there are differences in silica content and impurities in both types of ash, which may affect the stability of MOF-5, affecting the performance of MG removal. Until now, no report has been incorporating the silica from industrial burning waste such as RHA and CFA into MOF-5 in the adsorption of MG nor any isotherm and kinetic studies. Thus, it is worthwhile to be investigated.

1.3 Research Objectives

1. To synthesise and study the effect of incorporating different types and content of silica from RHA and CFA into MOF-5 in enhancing MG dye removal.
2. To study the MG dye adsorption on modified MOF-5 under various operating conditions (adsorbent amount, contact time, solution pH, shaking rate, temperature, and initial dye concentration).
3. To study the batch adsorption isotherm and kinetics of MG dye adsorption on modified MOF-5.

1.4 Scope of Study

The application of the modified MOF-5 in the adsorption of MG dye from wastewater has been widely studied due to its adsorption efficiency. Thus, understanding the parameters that affect the adsorption performance of MG dye is crucial. The scope of this study is to determine the optimum operating parameters of MG dye adsorption, such as initial dye concentration, shaking rate, temperature, solution pH, adsorbent amount, and contact time. Furthermore, the various modification of MOF-5 is also one of the factors of adsorption efficiency. The pristine MOF-5 was firstly synthesised, followed by the RHA and CFA modification. The preliminary test was conducted to compare the performance of each variety of modified MOF-5. The modified MOF-5 with the best performance was used to continue the operating parameters study. The optimum and reasonable parameter was used to proceed with the following factors. The data plotting was used to observe the trend and determine the adsorption isotherm and kinetics during the MG dye adsorption. Lastly, characterisation was carried out to determine the properties and capability of the modified MOF-5.

CHAPTER 2

LITERATURE REVIEW

2.1 Removal of Dye from Wastewater

There are various applied methods of dye removal from wastewaters. Typically, the methods are grouped into three categories shown in Table 2.1.

Table 2.1 Methods of Dye Removal from Wastewater.

Categories	Methods	References
Physical	Adsorption	(Altintig et al., 2018)
	Ion Exchange	(Liu et al., 2007)
	Membrane Filtration	(Ahmad et al., 2002)
	Coagulation/Flocculation	(Guibal and Roussy, 2007)
Chemical	Fenton's Reagent Technique	(Patil and Raut, 2014)
	Ozonation	(Wijannarong et al., 2013)
	Photocatalytic	(Muruganandham and Swaminathan, 2006)
Biological	Aerobic Degradation	(Buitrón et al., 2004)
	Anaerobic Degradation	(Xiao et al., 2018)

Adsorption is a process which utilises the surface forces where the atoms, ions, or molecules from a gas, liquid, or dissolved solid adhere to a surface. Adsorbents are solids used to adsorb gases or dissolved chemicals, whereas adsorbates are usually called adsorbed molecules. Generally, adsorbents are highly porous and have large surface areas to enhance adsorption efficiency. It is one of the most popular processes used in chemical engineering to separate pollutants from wastewater. In this application, since the adsorbents are required to remove the dye from the wastewater,

thus, it is known as liquid-phase adsorption. There are various derived adsorbents, such as charcoal, waste resources, ores, and zeolites. The waste resources include sawdust, algae, fruit wastes, rice husk, scrap tyres, peat, and wood chips (Cameselle et al., 2013). By comparing the advantages and disadvantages of the adsorbents for dye removal, activated carbon has good performance in the adsorption of various dyes. However, it is costly, wood chips have good adsorption capacity for acid dyes but require long retention times, and peat performs well due to its cellular structure. However, the specific adsorption surface area is lower than activated carbon (Robinson et al., 2001). However, the adsorption efficiency mainly depends on the nature of dye molecules, adsorbents and operating conditions. Scientists have derived numerous adsorption isotherms used to explain the data, such as Langmuir isotherm, Freundlich isotherm, BET isotherm, Temkin isotherm, Dubinin-Radushkevich isotherm, Kisliuk isotherm, Thomas isotherm, Frumkin isotherm, and Sips isotherm. Langmuir and Freundlich isotherms are the most common model used to predict the adsorption capabilities (Tewari et al., 2018).

Ion exchange is a common wastewater treatment method that involves exchanging one or more undesired ionic pollutants for other non-objectionable ionic substances. The contaminant and the exchanged substances must dissolve in the water and have the same electrical charge type, either positive or negative. In this case, this method is only applicable to ionic dyes. In industry, the manufacturers usually use resins or membranes for this process. The resins are tiny and microporous beads made of polystyrene and polyacrylate, which are insoluble in water and organic solvents. The ion exchange membrane is a unique idea which combines the electrochemical features of ion exchange resins and the membrane's permeability (Hassanvand et al.,

2017). Ion exchange can regenerate with no adsorbent loss, but it does not work for all types of dye (Robinson et al., 2001).

Membrane filtration usually occurs in tertiary wastewater treatment. It includes microfiltration, ultrafiltration, and nanofiltration. Typically, larger particles and biologically degraded products are removed using microfiltration or ultrafiltration membrane techniques (Van der Bruggen et al., 2005; Fersi et al., 2005). A nanofiltration membrane with nano-sized pores is used to separate salt solutions that comprise monovalent cations and anions from dye effluent. Fouling happens regularly in membrane-technique operations. Some efforts are done to manage fouling problems such as pre-treatment stages of wastewater, changing and optimising the membrane separation conditions such as the inlet solution composition, membrane properties, and hydrodynamics condition (Thamaraiselvan and Noel, 2015). Membrane filtration removed all types of dyes but produced concentrated sludge (Robinson et al., 2001).

Fenton's reagent is a mixture solution that consists of hydrogen peroxide and ferrous ions as a catalyst. Hydrogen peroxide is a strong oxidising agent that dissociates hydrogen and hydroxyl radicals. Therefore, Fenton's Reagent technique is an advanced oxidation process (AOP). In this process, the hydroxyl radicals produced from the reagent will oxidise and degrade the specific organic compounds of the dyes. With this, the wastewater's chemical oxygen demand (COD) could be reduced before being channelled to the environment (Patil and Raut, 2014). Fenton's reagent technique has the advantage of effective decolourising soluble and insoluble dyes. It can decolour a wide variety of wastes, but this method will generate sludge and is prohibitively expensive (Robinson et al., 2001). Other than this, ozone is another strong oxidising agent, and the process is known as ozonation, which is considered one of the AOPs. Ozonation can be operated under gaseous conditions without any

increment of wastewater and sludge volume but with a short half-life, around 20 minutes (Robinson et al., 2001).

2.2 Adsorption of Malachite Green Dye from Wastewater

Among the techniques mentioned above, adsorption is highly proposed and appealed to due to its high efficiency, simplicity, and low cost (Albadarin et al., 2017; Naushad et al., 2018). This technique is well-known for producing high-quality output water by removing dissolved organic pollutants such as dyes (Walker and Weatherley, 1998; Zhu et al., 2020). Although many nations have banned the use of MG dye owing to its major negative effects, it is still used in various industrial operations such as fish farming and textile dyeing due to its low cost and ease of availability. Many studies have been done on various types of adsorbents for the MG dye removal from wastewater, where the types of adsorbents are shown in Figure 2.1. The adsorbents are generally divided into five major types: activated carbon, non-conventional low-cost, nanomaterial, composite and nanocomposite, and miscellaneous.

Activated carbon (AC) is a well-known effective adsorbent due to its microporous structure, large surface area, and high surface reactivity. However, these adsorbents are costly due to their high manufacturing costs. Generally, AC is classified into two types: commercial AC and agricultural waste-derived AC. Although the US Environmental Protection Agency has claimed that AC is one of the best possible control strategies, its broad application is limited due to its expensive cost (Raval et al., 2016a).

With this, the researchers have attempted to find non-conventional low-cost alternative adsorbents to reduce the treatment costs. For instance, waste materials from agriculture and industry, natural materials (including clays, siliceous materials, and

zeolites), and bio-sorbents (including biomass, biopolymer, and peats) (Raval et al., 2016c). Generally, agricultural and industrial solid wastes are cheap and abundant. Due to their physicochemical properties, the utilisation of these wastes can potentially impact the national economy (Crini, 2006). On the other hand, clays possess a sheet-like arrangement and are made up of octahedrally and tetrahedrally ordered silicates and aluminates that are usually bound with water. Siliceous materials are sedimentary rocks mainly made of silica; zeolites are porous crystalline aluminosilicates with tetrahedrally linked three-dimensional frameworks and extra-framework charge balancing cations. Other than that, biomass is the biological substance derived from living organisms or their parts, whereas biopolymers are molecules with a high molecular weight that come from living creatures (Raval et al., 2016c).

Furthermore, the researchers also aimed at nanomaterials or nanocomposites, where the nano-scale inclusions are embedded into a material's matrix due to the attractive advantages of nanomaterials (Raval et al., 2016c; Chen et al., 2013). Due to the large ratio of surface to volume, these adsorbents show great performance in the bonding of waste. The nano-size of these adsorbents are easy to manipulate and can support various uses (Raval et al., 2016c). The comparison between various adsorbent types used for MG removal and their respective optimum operating conditions, including the solution pH, contact time, and adsorbent dosage, are tabulated in Table 2.2.

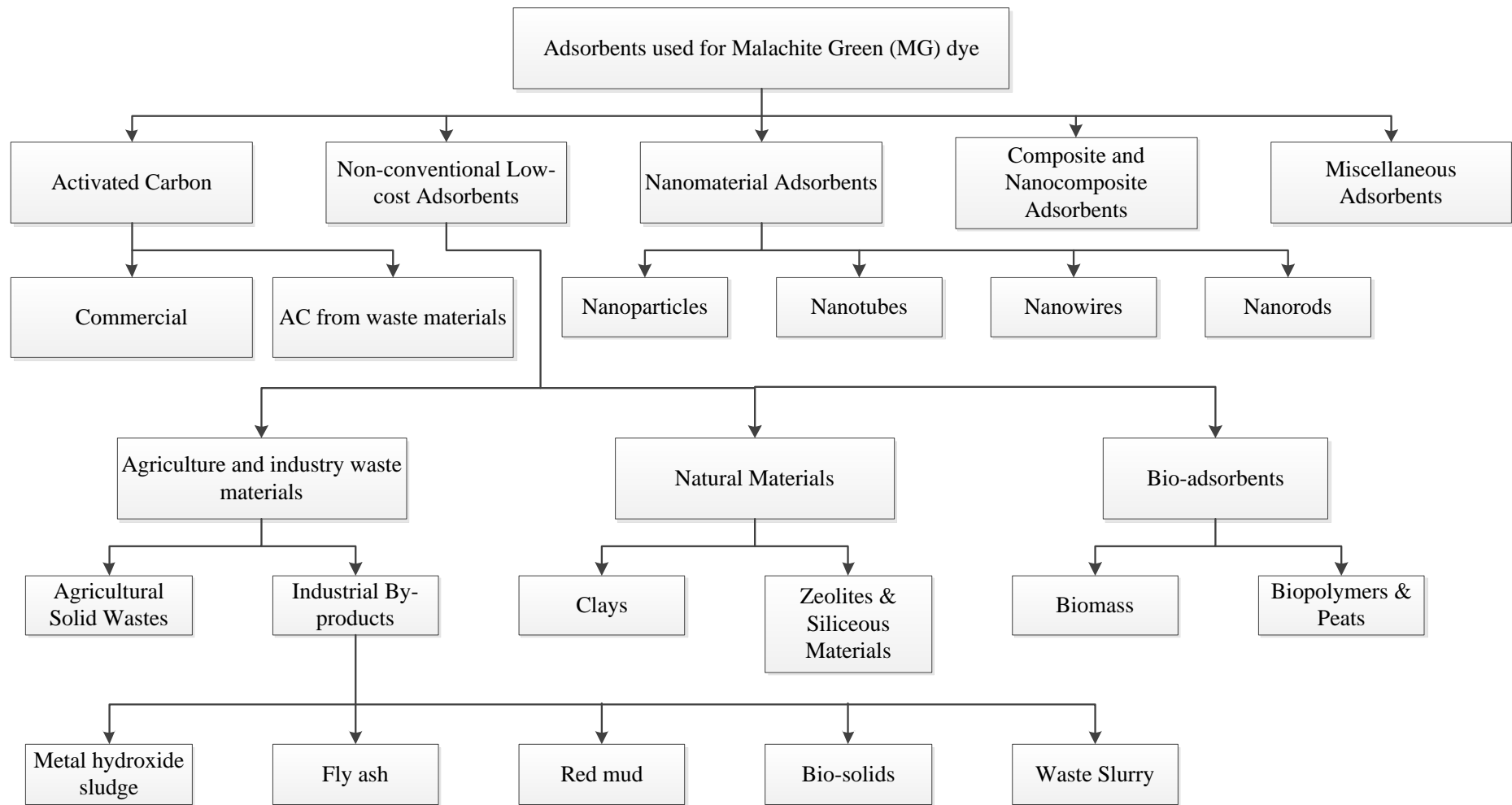


Figure 2.1 Classification of adsorbents used for MG removal (Raval et al., 2016c).

Table 2.2 Types of adsorbents and its adsorption capacity on MG dye removal.

No.	Adsorbent type	Experimental conditions					References	
		Q_{max}	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage
1.	Powdered AC	509.0	Langmuir and Redlich-Peterson	-	-	-	-	(Kumar, 2006)
2.	AC	490.8	Langmuir and Redlich-Peterson	Pseudo-second-order	-	-	-	(Kumar and Sivanesan, 2006)
3.	Coal-based AC	325.0	Freundlich	-	-	-	-	(Aitcheson et al., 2000)
4.	Commercially available powdered AC	222.2	Freundlich	-	-	15 mins	0.7 g/L	(Malik et al., 2007)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time	
5.	AC prepared from lignite	200.0	Langmuir	Pseudo-second-order	7	60 mins	0.1 g/50 mL (Önal et al., 2007)
6.	Laboratory grade AC	42.2	Redlich-Peterson	Pseudo-second-order	7	240 mins	4 g/L (Mall et al., 2005)
7.	Acid-activated carbon	9.8	Langmuir	-	6	40 mins	- (Hema and Shanmugam, 2007)
8.	Activated charcoal	0.2	Langmuir	-	7	30 mins	0.1 g (Iqbal and Ashiq, 2007)
9.	Polygonum orientale Linn AC	556.0	Langmuir	Pseudo-second-order	10	150 mins	0.45 g/L (Wang et al., 2010)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References	
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage
10.	Jute fiber carbon	136.6	Freundlich	Pseudo-second-order	8	220 mins	0.05 g	(Porkodi and Vasanth Kumar, 2007)
11.	Bamboo-based AC	263.6	Langmuir	Pseudo-second-order	4	170 mins	0.2 g	(Hameed and El-Khaiary, 2008b)
12.	Rambutan peel-based AC	329.5	Freundlich	Pseudo-second-order	8	24 hr	0.2 g	(Ahmad and Alrozi, 2011)
13.	Spent tea leaves AC	256.4	Langmuir	Pseudo-second-order	4	-	0.8 g/L	(Akar et al., 2013)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time	
14.	AC prepared waste apricot	163.9	Langmuir and Frumkin	-	-	60 min	0.1 g/50 mL (Başar, 2006)
15.	Rice husk AC	63.9	Langmuir	Pseudo-second-order	-	40 mins	- (Sharma and Singh, 2009)
16.	Banana (Musa paradisiaca) stalk-based AC	141.8	Langmuir	Pseudo-second-order	8	120 mins	0.2 g (Bello et al., 2012)
17.	Eggshells	243.2	Freundlich	-	6	-	1.0 g/L (Podstawczyk et al., 2014)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					Referencesv
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time	
18.	Water nut modified carbon	46.3	Langmuir	Pseudo-second-order	8	-	10 mg/ 50 mL (Ahmad and Mondal, 2010)
19.	Treated ginger waste	188.6	Langmuir	Pseudo-second-order	9	150 mins	0.5 g (Ahmad and Kumar, 2010)
20.	Breadnut peel	180.0	Freundlich	Pseudo-second-order	8.02	240 mins	- (Chieng et al., 2014)
21.	Pomelo (Citrus grandis) peels	178.4	Langmuir	Pseudo-second-order	8	240 mins	0.2 g (Bello et al., 2012)
22.	Oil palm trunk fiber	149.4	Langmuir	Pseudo-first-order	8	195 mins	0.3 g (Hameed and El-Khaiary, 2008a)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References	
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage
23.	Bagasse fly ash	170.3	Freundlich	Pseudo-second-order	7	240 mins	1 g/L	(Mall et al., 2005)
24.	Activated slag	74.2	Langmuir and Freundlich	Pseudo-first-order	10	6-8 hr	1 g/L	(Gupta et al., 1997)
25.	Fly ash	40.7	Langmuir	Pseudo-second-order	>6	-	2 g/L	(Witek-Krowiak et al., 2012)
26.	Bentonite	178.6	Langmuir	Pseudo-second-order	5	60 mins	1 g/L	(Bulut et al., 2008)
27.	Kaolin	65.4	Langmuir	Pseudo-second-order	7	90 mins	2 g/L	(Nandi et al., 2009)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References	
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage
28.	Zeolite	46.4	Langmuir	Pseudo-first-order	6	-	-	(Wang and Ariyanto, 2007)
29.	Tetrahedral silica	45.1	Langmuir	-	6	5 hr	150 mg/ 50 mL	(Kannan et al., 2008)
30.	Pithophora sp., a fresh water algae	117.7	Redlich-Peterson	Pseudo-second-order	5	8 hr	0.015 g	(Kumar et al., 2005)
31.	Freshwater macrophyte alligator weed	185.5	Langmuir	Ritchie-second-order	6	-	7.0 g/L	(Wang, 2009)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References	
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage
32.	Ashoka (Saraca asoca) leaf powder	83.3	Freundlich	Pseudo-second-order	6	25 mins	2.0 g/L	(Gupta et al., 2012)
33.	Native anaerobic granular sludge	61.7	Langmuir	Pseudo-second-order	5	2 hr	2.4 g/L	(Cheng et al., 2008)
34.	Daucus carota plant (carrot stem powder)	43.4	Freundlich	Pseudo-second-order	7	30 mins	2.0 g/L	(Kushwaha et al., 2014)
35.	NiO nano flake-based flowerlike architectures	142.1	Langmuir	Pseudo-second-order	-	-	333.3 mg/L	(Wei et al., 2014)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time	
Functionalized multi							
36.	wall carbon nanotubes (f-MWCNTs)	142.9	Langmuir	Pseudo-second-order	7	80 mins	0.08 g/100 mL (Shirmardi et al., 2013)
Silver nano particles							
37.	(AgOH-NP) loaded on AC prepared from Rosa canina	105.0	Freundlich	Pseudo-second-order	8	20 mins	0.09 g/50 mL (Tavakol et al., 2015)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References
		Q_{\max}	Isotherm model	Kinetics model	pH	Equilibrium time	
Superparamagnetic							
38.	sodium alginate-coated Fe ₃ O ₄ nanoparticles	47.8	Langmuir	Pseudo-second-order	9	20 mins	0.1 g/50 mL (Mohammadi et al., 2014)
Zeolitic imidazole							
39.	framework-67 (ZIF-67)	3227.0	Langmuir	Pseudo-second-order	-	2 hr	0.25 g/L (Lin and Chang, 2015)
40.	Graphite oxide (GO)	248.0	Langmuir	Pseudo-second-order	-	20 mins	10 mg/500 mL (Bradder et al., 2010)

Table 2.2 Continued.

No.	Adsorbent type	Experimental conditions					References	
		Q_{\max}^a	Isotherm model	Kinetics model	pH	Equilibrium time		Adsorbent dosage ^b
41.	Poly- γ -glutamic acid	293.3	Redlich-Peterson	Pseudo-second-order	>5	2 hr	0.4 g/L	(Stephen Inbaraj et al., 2006)
42.	Defective coffee beans press cake	208.3	Langmuir	Pseudo-second-order	5	4 hr	5.0 g/L	(Franca et al., 2010)

a: the maximum adsorption capacity of adsorbent (mg/g)

b: the mass of the adsorbent contained in each volume of MG aqueous solution