DECOLOURIZATION OF BRILLIANT GREEN DYE IN AQUEOUS MEDIA BY USING MODIFIED MOF-5 ADSORBENT

by

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LIST OF SYMBOLS

Symbol	Description	Unit
Ce	concentration equilibrium	mg L^{-1}
C_t	concentration of dye at specific time	mg L^{-1}
h	half adsorption	mg g^{-1}
K_1	Kinetic value for Langmuir model	min^{-1}
K_2	Kinetic value for Freundlich model	mg g^{-1} min^{-1}
K_L	Langmuir constant	L mg^{-1}
K_f	Freundlich constant	mg g^{-1}
LC_{50}	Lethal concentration	mg L^{-1}
m	mass adsorbent	g
n	measure of intensity	-
Q_t	adsorption capacity at specific time	mg g^{-1}
Q_e	Equilibrium adsorption capacity	mg g^{-1}
Q_m	maximum adsorption capacity	mg g^{-1}
R^2	determination coefficient	-
t	time	min
$t_{1/2}$	half adsorption time	mg g^{-1}
T	temperature	ºC
V	volume	L

LIST OF ABBREVIATION

Symbol	Description
As(V)	Arsenate
AMX	Amoxicillin
BET	Brunauer-Emmet-Teller
BDC	benzenedicarboxylate
BG	Brilliant green
COD	Chemical oxygen demand
CFA	Coal fly ash
CNS	Cashew nut shell
Cu-BTC	Copper-paddlewheel-based MOF
DES-RHA	Deep eutectic solvent – rice husk ash
DMF	N,N-dimethylformamide
EDX	Energy dispersive X-ray
FA	Fly ash
FAG	Fly ash goethite
Fe_3O_4@MOF-5	magnetic MOF-5
FTIR	Fourier transform infrared
KOH	Potassium hydroxide
MB	Methylene blue
MO	Methylene orange
MOF	Metal organic framework
MS	Meossbauer spectroscopy
NPC	Nitrogen-doped porous carbon
PAC	Powder activated carbon

RH	Rice husk
RHA	Rice husk ash
RhB	Rhodaime
SEM	Scanning electron microscope
TiN-WN	Titanium nitride and tungsten nitride
TiO_2	Titanium dioxide
UV	Ultraviolet
XRD	X-Ray Diffraction
$Zn(OH)_2$	Zinc hydroxide

PENYAHWARNAAN PENCELUP HIJAU BRILLIAN DALAM MEDIUM AKUEUS DENGAN MENGGUNAKAN PENJERAP 'MOF-5' YANG DIUBAHSUAI

ABSTRAK

Penyelidikan ini adalah berkenaan penyahwarnaan pencelup hijau brillian (BG) dengan menggunakan pelbagai perjerap yang diubahsuai; kerangka logam organic (MOF-5) asli, MOF-5 disalut dengan abu arang batu (CFA) dari kilang, MOF-5 disalut abu sekam padi yang dibakar pada suhu berbeza RHA_{500} dan RHA_{900}, serta MOF-5 disalut dengan campuran RHA_{900} dan CFA dari kilang yang berbeza nisbahnya. Bahan penjerap digunakan untuk kajian penjerapan pada masa sentuhan, jumlah penjerapan dan kepekatan awal pewarna yang berbeza tetapi kadar gegaran malar (200 rpm) dan suhu (30 ºC) yang tetap. Pengubahsuaian MOF-5 yang disalut RHA_{900} mempunyai keupayaan penjerapan yang lebih tinggi terhadap pencelup BG. Penyahwarnaan pencelup BG yang tinggi, kira-kira 92% boleh berlaku dengan menggunakan 1.4 g penjerap jenis MOF-5@ disalut RHA_{900} selama 2 jam. Penyahwarnaan pencelup BG meningkat apabila masa sentuhan bertambah, kepekatan pewarna awal berkurang dan kuantiti penjerap bertambah. Kinetik penjerapan dibandingkan berdasarkan model pseudo-tertib pertama dan pseudo-tertib kedua manakala isoterma dianalisis berdasarkan model Langmuir and Freundlich. Kedua-dua kinetik dan isoterma dipilih berdasarkan data penjerapan yang terbaik. Ciri bahan penjerap MOF-5 yang terpilih telah dianalisa dengan menggunakan pembelauan sinar-X (XRD) untuk mengenal kristal, mikroskop electron pengimbasan (SEM) untuk mengkaji bentuk dan morfologi, Brunauer-Emmet-Teller (BET) untuk mengkaji sifat dan FT-IR untuk mengenal pasti perubahan kumpulan berfungsi. Penjerap MOF-5@RHA_{900} mempunyai permukaan BET yang lebih tinggi (91.6810 $m^2\ g^{-1}$) berbanding MOF-5@CFA_f (3.4651 $m^2\ g^{-1}$),

yang boleh membenarkan kadar penyingkiran pewarna BG yang lebih tinggi. Struktur meso-liang penjerap MOF-5@RHA_{900} dan MOF-5@CFA_f telah dibuktikan melalui analisis taburan liang.

DECOLOURIZATION OF BRILLIANT DYE IN AQUEOUS MEDIA BY USING MODIFIED MOF-5 ADSORBENT

ABSTRACT

This research is mainly about the decolourization of brilliant dye by using different type of modified adsorbent, pristine Metal Organic Framework (MOF-5), MOF-5 coated with coal fly ash (CFA) from factory, MOF-5 coated with rice husk ash (RHA) from factory, MOF-5 coated with RHA_{900}, MOF-5 coated with RHA_{500}, as well as MOF-5 coated with different ratio of mixed RHA_{900} and raw CFA from factory. The synthesized adsorbents were used for adsorption study at different contact time, adsorbent amount and initial dye concentration but constant shaking rate (200 rpm) and temperature (30 ºC). Modified metal organic framework (MOF-5) coated with RHA_{900} has a higher adsorption capability towards the brilliant green (BG) dye. A high removal of BG dye which is about 92% could be occurred by using 1.4 g of MOF-5@RHA_{900} adsorbent shaking time of 2 hours. The removal of BG dye increases with the increasing of contact time, decreasing initial dye concentration and increasing of adsorbent amount. The kinetic of the adsorption was compared based on pseudo-first-order and pseudo-second-order models while the isotherm was analyzed based on Langmuir and Freundlich models. Both kinetic and isotherm model were choose based on the best fitted adsorption data. The adsorption kinetic obeyed the pseudo-second-order model while the adsorption isotherm followed the Langmuir Isotherm model. The characterization of the prepared and spend modified MOF-5 adsorbents were analyzed by using X-ray diffraction (XRD) to identify structure of the crystal, scanning electron microscope (SEM) to study the shapes and morphologies, Brunauer-Emmet-Teller (BET) to identify physical properties and FT-IR test to identify the changes of the functional group. MOF-5@RHA_{900} adsorbent has a higher BET surface (91.6810

m^2 g^{-1}) compared to MOF-5@CFA_f (3.4651 m^2 g^{-1}), which could allow higher rate of BG dye removal. The mesopore structure of MOF-5@RHA_{900} and MOF-5@CFA_f adsorbent had been proved by the analysis of pore distribution.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the research background, problem statement, objective, and scope of study for the adsorption of brilliant green dye.

1.1 Research Background

In this rapid growing industry, the earth seems to be very sick to face the increasing amounts of pollutant discharged to the environment, especially to the natural water. One of the common pollutants is dye, which usually discharge together with the untreated wastewater. Generally, there two types of dyes which are organic and synthetic dye. It is estimated that approximately 700,000 tons of synthetic dye are produced annually, and the commercially used worldwide is more than one hundred thousand types (Adar, 2020). By comparing few methods of removing dye from aqueous solution, it is observed that adsorption has the highest performance with easy operation.

Adsorption involves the use of adsorbent, microporous solid to allow the dye or adsorbates to adhere to its surface. The adsorbent will create a molecular film due to existence of balanced on the surface of liquid and usually has creates the Van der Waals forces or covalent bond with the adsorbates. Metal Organic Frameworks (MOFs) is a new class of porous structures and consists of highly ordered crystalline materials prepared by self-assembly of metal ions with organic linkers to yield low density network structures of diverse topology (Hu et.al., 2013). The first robust of MOF is MOF-5 which have special structure that contributes to large surface area, an exceptionally large pore volume, and relatively high thermal stability (Zheng et.al., 2014). However, in the last few years many researchers conducted study related to modified MOF-5 to improve its stability and optimize the selectivity. Poor thermal

stability and inadequate Bronted acid are drawbacks of traditional metal-organic frameworks (MOFs), which greatly limit their use, especially in high temperature and pressure reactions such as carbohydrate dehydration (Chatterjee et.al., 2018). Meanwhile, the addition of magnetic compound acts as an alternative way because the powdery magnetic material from solution can be easily separated by using an external magnet without filtration or centrifugation procedures (Hao et.al., 2016).

1.2 Problem Statement

Nowadays, most of the textile industry in Malaysia contribute to the production of dye wastewater which could be harm to the environment. The ionic charge on the molecules of dye used to categorized the dyes as anionic, cationic, non-ionic or zwittericonic. Brilliant Green (BG), that are classified as cationic dye are usually used for various purposes such as biological stain, veterinary medicine and also an additive to poultry feed (Nandi et.al., 2009). The resistivity properties of dye is a serious concern to the environmental aesthetic pollution due to its toxicity (Kismir and Aroguz, 2011). It should be separated or remove from the aqueous solution by using physical, chemical or biological methods, depends on the nature and quantity of the dyes.

Adsorption should be the best choice for acid dye removal as it operates at low operating temperature and quite simple procedure. However, earlier adsorption method which usually use activated carbon as the adsorbent leads to narrow application because they are difficult to regenerate and also high production cost (Li et.al., 2013). Metal Organic Framework - 5 (MOF-5) adsorbent seems to be effective at removal of brilliant green dye but, some modifications are needed to improve its stability and adsorption efficiency since the pristine MOF-5 has low efficiency The addition of compound with high carbon and silica content that will increase its stability

but somehow leads to increasing of operational cost. Instead of using new raw material, it would be more practical to use waste substances generated by combustion process such as coal fly ash or rice hush ash. Although the fly ash has been utilized in the manufacture of cement and concrete, the sort of large quantity of strong waste hassle can't be virtually solved with the aid of using the disposal into the landfill (Chatterjee et.al., 2018). Another problem is the unmodified MOF-5 cannot be easily separated from the solution and need either filtration or centrifugal procedures, which also increase the overall cost. To ensure the modified MOF-5 functioning well and analyse the optimum condition for adsorption process, it is important to study the factor that affecting it. The main factors that affecting the adsorption process are pH of solution, adsorbent dosage, adsorbent particle size, contact time, temperature and adsorbate concentration.

1.3 Objectives

The objectives of this project are:

1. To investigate the adsorption of brilliant green dye using modified MOF-5 by varying the contact time, dye concentration and adsorbent amount.
2. To study the kinetic and isotherm of brilliant green dye adsorption by using modified MOF-5.
3. To analyze the characteristic of the prepared and spent modified MOF-5 adsorbent by using different equipments.

1.4 Scope of study

The adsorption studies will be carried out to evaluate the effect of few parameters towards the removal of brilliant green dye by using modified metal organic framework (MOF-5). This research will be focusing on the synthesis of modified MOF-5 with different ratio of coal fly ash, rush husk ash and magnetic Fe_3O_4. To investigate the efficiency of the adsorbents, the adsorption studies will be observed by varying the contact time, dye concentration and adsorbent amount. The concentration of the brilliant green dye can be analyzed by using UV-spectrophotometer, wavelength of 623 nm. The characterization of the prepared and spend modified MOF-5 adsorbent will be analyzed by using X-ray diffraction (XRD) to identify structure of the crystal, scanning electron microscope (SEM) to study the shapes and morphologies, Brunauer-Emmet-Teller (BET) to identify physical properties and FT-IR test to identify the changes of the functional group.

CHAPTER 2

LITERATURE REVIEW

This chapter involves the overview of brilliant green dye, comparison of removal dye method, factor affecting the removal of dye and sustainability due to the use of waste material. Important information related to the characterization was also represented for a better understanding before carried out the adsorption study.

2.1 Brilliant Green Dye

The increase in utilizing of synthetic industrial dyes have significantly pollutes water bodies raising serious concerns about their large-scale use (Singh et.al., 2022). The complex structure of dyes makes them difficult to degrade, whereas leads to the use of expensive energy-intensive process (Mogale et.al., 2022). However, an alternative method, the adsorption technique was found to be an effective way to remove pollutants because of its cost, efficiency and simplicity. Generally, dyes are designed to be sufficiently stable compounds that are not easy to be degraded and results in depletion of dissolved oxygen, making a bad impact for the aquatic life forms. There are about 15% of dyes used in textile dyeing industry do not attach to the fibres, so that resulting to colour effluent and a serious water pollution when release to the wastewater (Dellamatrice et.al., 2017). Figure 2.1 shows the discharge percentage of dye mixture from each process of the textile industry, whereby dyeing recorded the highest value. 85% of the total amount of dye mixture prepared at the beginning of the dyeing process is discharged as waste (Katheresan et.al., 2018).

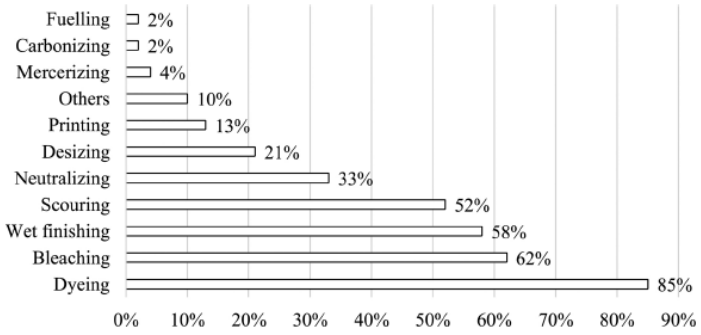

Figure 2.1 Percentage of dye mixture from each process of the textile industry discharged as waste (Katheresan et.al., 2018)

Brilliant green dyes are widely used in printing paper and textile industries. Brilliant green is an organic hydrogensulfate salt, with the attachment of 4-{[4[(diethylamino)phenyl]methylidene}-N,N-diethycyclohexa-2,5-dien-1-iminium as the counterion and molecular formula of $C_{27}H_{33}N_2^+$ (National Center for Biotechnology Information., 2022). The molecular structure of brilliant dye is depicted in Figure 2.2.

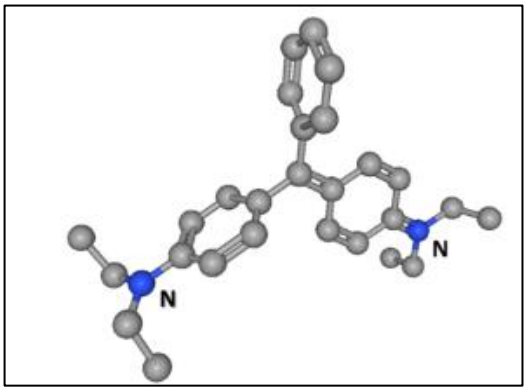

Figure 2.2 Schematic structure of Brilliant Green dye (Mathioudakis et.al., 2021)

According to Nandi et.al (2009), BG dye is one of the commonly known cationic dye, that are used for various purpose. It has major consequences in human health, causing damage to renal tissues and reproductive systems (Basharat et.al.,

2021), and toxic to lungs through inhalation (Kismir and Aroguz, 2011). Perhaps, carbon dioxide, sulphur oxides and nitrogen oxides may be produced during its breakdown (Kismir and Aroguz., 2011), which results to a serious environmental damage. A study of decolourization of wastewater by Hao et.al (2000) showed that cationic dyes are more toxic (e.g., LC_{50} for Basic Violet 1 is only 0.05 mg L^{-1} to *P.Promelas*), followed by anionic dyes, and the least toxic is direct dye (LC_{50}>180 mg L^{-1}). A high value of LC_{50} indicates a low toxicity of dyes. However, activated sludge does not reduce the toxicity of textile waste, probably because it is nonbiodegradable compounds (Hao et.al., 2000). Meanwhile, activated carbon is not cost effective as it commonly produced from very expensive material which are not renewable, and has some environmental consequences (Mansour et.al., 2020).

2.2 Adsorption process of dye removal

Brilliant dye is highly toxic for human, aquatic system and also gram-positive bacteria (Bose et.al., 2021). Therefore, the degradation or removal of dye from wastewater is very important before released to the environment, to avoid any pollution. There are many methods available for the removal of brilliant green dye, such as electrocoagulation (Márquez et.al., 2022), oxidation (Bose et.al., 2021), membrane-based separation (Bhaumik et.al., 2022) and adsorption (Nandi et.al., 2009). Table 2.1 showed the advantages and disadvantages of various physical removal method. By considering all methods of dye removal, adsorption process seems to be the best approach due to its lower price (Nandi et.al., 2009), high efficiency, ability to remove many chemical compound and simplicity of design (Mansour et.al., 2020). Adsorption has been considered the most appropriate procedure for the remediation of dyes and pharmaceuticals in wastewater (Zango et.al., 2021). Adsorption method

would be great as it permits reuse and recycle of the dyestuff and adsorbent. Utilization of physical techniques like adsorption for the removal of dyes from the effluents ends up being a monetarily feasible technique for a mass treatment option (Akshaya et.al., 2018).

Table 2.1 Advantages and disadvantages of various removal dye method (Nandi et.al., 2009; Bose et.al., 2021; Márquez et.al., 2022; Bhaumik et.al., 2022)

Method	Description	Advantages	Disadvantages
Adsorption	Use of adsorbent to adsorb dye molecules	High efficiency, ability to remove many chemical compound, simple design, economic fleasibility	Adsorbent can be costly
Electrocoagulation	Use of metallic coagulants, by sweeping coagulation encapsulating of dyes with agglomerates. Clumps can be	Allow the chemical oxygen demand (COD) from 70 to 90% Reproducible of hydrodynamics Easy to scale up	Generation of high amounts of sludge

Table 2.1 Continued.

	removed through filtration		
Oxidation	Irradiation of dye by using probe sonicator possessed with ultrasonic frequency	Sonocatalyst enhance the catalytic activity	Uneconomical due to high energy demands Prolong treatment time
membrane-based separation	Metallic nanoparticles supported on porous matrices as heterogeneous catalyst for Fenton-like reaction towards degradation of contaminants	Enhance catalytic activity	Synthesis of nanocarbon based support are cost intensive and produce environmental hazardous compounds, production of sludge

Furthermore, Table 2.2 showed the comparison of few studies on the removal of dyes. Chen and Tseng (2022) studied the synthesis of titanium nitride and tungsten nitride (TiN-WN) composition particles for selective adsorption of methylene blue (MB) dyes in water. The Tin-Wn composites show a selective MB adsorption under dark situation along with a photocatalytic behaviour under visible light irradiations. It was approximately 90% of MB removal within 90 mins and concentration of 10 - 5 M

by tuning the adsorbent composition. The adsorbent particles also showed a better removal of dye compared to anionic methyl orange (MO).

According to the Chen et.al (2018), the main criteria for selection of adsorbents are cost effectiveness, availability and adsorptive properties, as well as high surface area and reactive surface atom. The adsorption capacities of nitrogen-doped porous carbon (NPC) for MB was 626.1 $mg.g^{-1}$, the highest one compared to rhodaime B (RhB) and MO, 620.7 $mg.g^{-1}$,and 370.8 $mg.g^{-1}$ respectively. Large surface area, microporous structure and high-level surface activities leads to a good adsorption performance of porous carbon (Gor et.al., 2012).

Liu et.al (2016) study the adsorption of MB, MO and Rhb, similar as Chen et.al (2018) but using Polyoxometalate-based metal organic framework as adsorbent. The adsorption ability towards MB and RhB (97% and 68%, respectively) were higher than anionic dye MO (only 10%). Thus, it can be concluded that polyoxometalate with high negative charges played an important role in the adsorption process because of its stronger force with electropositive dyes.

To be clearer, the adsorption capacities of brilliant green dye were compared by using different adsorbent. Nandi et.al (2009) conducted a study of brilliant green removal on kaolin, dependency of various operating parameter and observation of its characterization. Maximal adsorption percentage, 98% was observed at pH 7 for the initial concentration of 20 mg L^{-1}, and decrease to 2.67% when pH reduced to 2.85. The kaolin and brilliant dye are chemisorption rather than physical adsorption as they exist as anion and cation in aqueous medium, respectively (Nandi et.al., 2009).

Next is the Saklikent mud as the adsorbent for removal of brilliant green dye from aqueous solution as it has high efficiency. The adsorption capacity of this adsorbent changed from 9.2 mg.g-1 to 9.7 mg.g-1 by the increment of temperature

from 25ºC to 55ºC. The kinetic data also showed that the calculated value of maximum adsorption capacity was likely the same as the maximum adsorption capacity obtained from the experiment. At high temperature, R^2 for second order adsorption model recorded the highest value, represents the adsorption kinetics of BG.

Another study by Samiyammal et.al (2022) is the usage of active carbon prepared from cashew nut shell (CNS) with potassium hydroxide (KOH) activation as adsorbent. This study used the mixture of CNS and KOH at mass ration of 1:4 and 1:1, heated at 600ºC for about 2 hours with the presence of nitrogen atmosphere. As a result, BG dye fitted with Langmuir model with a maximum capacity of 243.90 mg g^{-1}.

Table 2.2 Comparison of study of dye removal

Adsorbent	Dye	Adsorption capacity	Reference
titanium nitritride and tungsten nitride (TiN-WN)	methylene blue rhodaime B methylene orange	626.1 mg.g^{-1} MB 620.7 mg.g^{-1} RhB 370.8 mg.g^{-1} MO	Chen and Tseng (2022)
Polyoxometalate-based metal organic framework	Methylene blue Rhodaime B Methylene orange	97% MB 68% RhB 10% MO	Liu et.al (2016)
Kaolin	Brilliant green	98%	Nandi et.al (2009)
Saklikent mud	Brilliant green	9.7 mg g^{-1}	Kismir and Aroguz (2011)
cashew nut shell (CNS) with KOH	Brilliant green	243.90 mg g^{-1}	Samiyammal et.al (2022)

2.3 Modified metal organic framework (MOF-5)

There are many adsorbents available in nowadays' industry such as zeolite-based adsorbent, activated carbons and metal organic framework (MOF), widely studied by global researchers. Regardless of the frequent use of adsorption in wastewater treatment, the commercial price of activated carbon still remains an expensive material (Sivamani and Grace, 2009). MOFs with tunable options, organic function, high thermal and mechanical stability, open metal sites in the skeleton, huge pore size and high surface area, yet additionally can be handily ready in a one-pot. MOF-5 is re-synthesised using an established method that reveals extraordinary formation mechanism in the form of nanoplatelets 5 to 10nm in diameter (Zheng et.al., 2014).

According to Zango et.al (2021), MOFs exhibited higher adsorption efficiency for methylene blue (90.59% and 97.97%) as compared to methyl orange (38.24% and 28.80% z) for both UiO-66(Zr) and NH2-UiO-66(Zr), respectively, demonstrating that the MOFs can viably adsorb cationic dye more when compared to the anionic dye. They observed that the MOF has higher adsorption capacity 2.6 times than the pristine UiO-66(ZR) because of its dominating mesoporous nature as compared to the micropores in the UiO-66(Zr), with kinetics process best depicted by pseudo-second request model, showing a chemisorption process.

Besides, MOFs has the advantages in terms of reusability. MOFs have stand to overcome the deficiencies of carbon-based permeable adsorbents, for example, graphene and CNTs which are generally plagued by difficulty in regeneration and reusability because of their lower densities (Zango et.al., 2021). It is observed that the crystalline structure of the MOF contributes to their high-water resistance stability for anionic dyes adsorption.

Among many types of adsorbents, MOF-5 displays considerable application in potential in many fields due to their unique properties compared to their corresponding bulk material. As reported by Greer et.al (2016), the synthesis of MOF-5 involves the addition of 4-(dodecyloxy) benzoic acid to suppressed the formation of OH^- anions. It is observed that ZnO twin crystal, $Zn_5(OH)_8(NO_3)_2.2H_2O$ nanoplatelets or known as intermediate compound in size of 10-20nm were found first in the growth process synthesis of MOF-5 (Zheng et.al., 2014). Then, a complete structure of MOF-5 will be formed, where the benzenedicarboxylate (BDC) links the octahedral subunits of $[Zn_4O]^{6+}$. This adsorbent act as hydrophobic, with unique properties of control system to exhibits separation process. The hydrophobic property has a significant contribution to the adsorption of dye because it maintains cohesion between non-polar or poorly soluble molecules with long carbon chains in a solution (Uflyand et.al., 2021).

2.4 Magnetic MOF-5

Magnetic nanoparticles possess large capacity and easy separation of the solid phase, which is excellent for wastewater treatment Hao et.al (2016). The magnetic MOF-5 can be prepared by the chemical coprecipitation method. According to Hao et.al (2016), the prepared Fe_3O_4@MOF-C showed a high explicit surface area and strong magnetism because of the presence of iron oxide nanoparticles. It is determined that the value of saturation magnetization of Fe_3O_4@MOF-C was 32,8 emu g^{-1}. In terms of reusability of the magnetic adsorbent, Hao et.al (2016) determined that the adsorbent can be reused 13 times without a huge loss of its adsorption efficiency.

2.5 Sustainability

The concentration of toxic pollutants from aqueous medium can be reduced by using many organic waste materials (Priya et.al., 2022). Sago waste, barley straw, rice husk ash and tea leaves are the examples of low-cost, natural and abundant agriculture waste (Kaur et.al., 2021). Based on the experimental study, it is observed that serious issues have been occurred to the surrounding environment due to disposal of rice husk ash content by land filling in open area (Priya et.al., 2022). An alternative way to dispose the waste, known as incineration method has the advantages of volume reduction and heat recovery, but there is still risk of releasing heavy metals into the atmosphere (Zhang et.al., 2022). Hence, the use of waste agriculture as raw material to synthesis adsorbents would be great to imply sustainability as it is low cost and helps to reduce the amount of waste disposed to the landfill.

2.5.1 Rice Husk Ash (RHA)

Adsorption can be completed by utilizing different adsorbing agents, two noticeable adsorbents are rice hush ash (RHA) and titanium dioxide (TiO_2) (Akshaya et.al., 2018). Generally, RHA comes from the burning of rice husk under controlled temperature and specific time. Based on Kaur et.al (2021), RHA was washed with warm water and dried at 70 overnight. Figure 2.3 shows the anticipated paddy production in Malaysia from 2010 to 2020. Rao et.al (2012) states that about 220 kg (22%) of hush is produced for every 1000 kg of paddy mill, and about 55 kg (25%) of rice husk ash (RHA) is generated when the husk undergoes combustion process. By referring to Figure 2.3, about 2,300 $x10^3$ tonnes of paddy produced in Malaysia for year 2020 and it is estimated that the production of RHA is about $127x10^3$ (25% of husk) is generated. The increment amount of rice husk ash indicates that the agricultural wastes will remain high in future and sustainable for a long time.

According to Pode (2016), the removal of RHA in landfills could be risky because of space limits and may cause a genuine serious environmental problem. For the production of RHA, rice husk (RH) is generally burn out in temperature range from 400 to 1000ºC for 2-5 hours. High amorphous silica ash with low amount of carbon content can be obtained from the combustion process in the range of 500 to 800ºC. The author also states that the silica will become sticky, the particles may agglomerate and tend to remain in the apparatus if the temperature to burn RH too high. Rao et.al (2012) also reported that RHA contains 85 to 90% of silica.

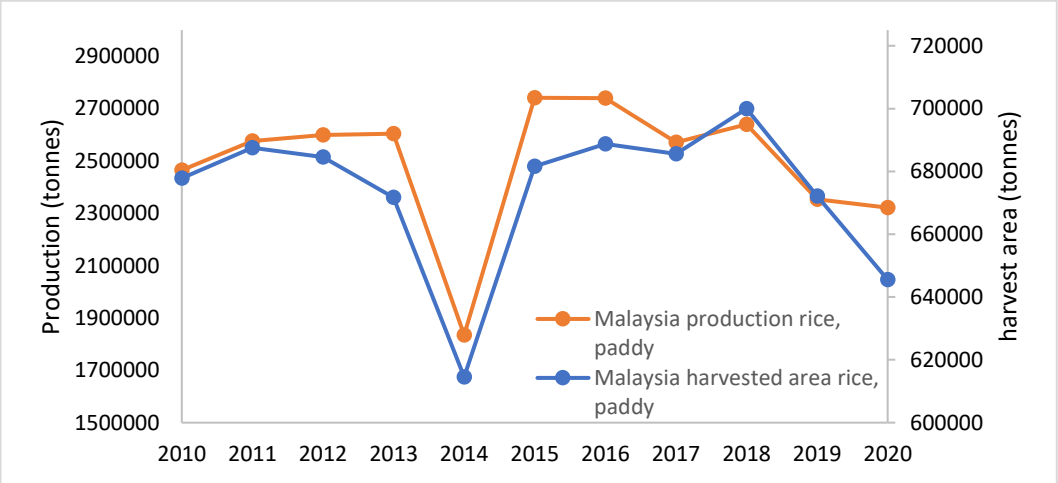

Figure 2.3 Production/yield quantities of rice, paddy in Malaysia

(https://www.fao.org/faostat/en/#country)

2.5.2 Coal Fly Ash (CFA)

Coal fly ash (CFA) is a solid waste generated in large amount worldwide, which required development of new methods for its productive reuse (Agarwal & Rani, 2017). The use of coal fly ash as an adsorbent would reduce the amount of disposed waste and encourage waste management, dominantly through resource recovery and act as

new added value and reuse of waste (Đolić et.al., 2021). It is stated that the chemical properties of fly ash are constrained by the contaminants contained in the combusted coal. The elements contained in fly ash (FA) and goethite impregnated fly ash (FAG) sample can be observed from Table 2.3, the results of energy dispersive x-ray (EDS) analysis. It is observed that the modified fly ash labelled as FAG is more efficient for the removal of Arsenate As(V) since the spent adsorbent contains higher amount of As. Huang et.al. (2020) utilized the coal fly ash as feedstock to produce high productive mesoporous material adsorbent through a simple one-step low-temperature alkali roasting method and use for Cd^{2+} adsorption.

Table 2.3 EDS analysis of the FA/As and FAG/As adsorbents (Đolić et.al., 2021)

Element	Adsorption As(V) on FA		Adsorption As(V) on FAG	
	Element (%)	Atomic (%)	Element (%)	Atomic (%)
O	54.43	72.03	53.91	72.88
Al	8.66	6.79	7.83	6.27
Si	17.64	13.29	15.30	11.78
P	0.36	0.24	0.35	0.25
K	0.70	0.38	0.68	0.38
Ca	2.30	1.22	2.56	1.38
Ti	0.38	0.17	0.28	0.13
Fe	15.39	5.84	14.45	5.60
As	0.14	0.01	4.62	1.33

2.6 Batch Adsorption Study

To identify the efficiency of adsorbent towards the removal of dye, many researchers have been carried out the batch and kinetic adsorption studies. Langmuir isotherm model is used in adsorption study by assuming that adsorption is limited to monolayer and occurs on homogeneous sites within the adsorbent (Nadiye-Tabbiruka et.al., 2018). According to Langmuir model, the adsorption occurs uniformly on the active sites of the adsorbent, which means that no further adsorption can take place at the site once adsorbate occupied it (Oguz et.al., 2006). The comparison of

Langmuir and Freundlich isotherm models for dye adsorption can be made by using non-linear regression. Based on Table 2.4, the data of adsorption isotherms constants of the Copper-paddlewheel-based MOF (Cu-BTC) samples by Lin et.al, (2014), the coefficient of determination fitted to Langmuir isotherm was higher than that of Freundlich isotherm model. The equation for the line of best fit obtained for the Langmuir model showed a more prominent coefficient of determination than the Freundlich model, demonstrating homogeneity of the surface of the adsorbent material and the development of a monolayer of azo dye species covering the surface of the adsorbent (Santos et.al., 2017). There are abundant of vacant sites on the material surface at the beginning of the adsorption period, which caused a fast adsorption rate a of Cd^{2+} (Huang et.al., 2020). Furthermore, the adsorption of dye by using specific adsorbent could also be affected by few factors such as pH of solution, adsorbent dosage, adsorbent particle size, contact time, temperature and adsorbate concentration.

Table 2.4 Langmuir and Freundlich isotherm constants of the Cu-BTC samples (Lin et.al., 2014)

Adsorption isotherm	constants	298 K	308 K	318 K
Langmuir equation	$Q_{m,c}$ (μmol g^{-1})	15.28	11.79	11.10
	K_L(L μmol^{-1})	0.6048	1.2387	1.3194
	R_L	0.1419	0.0747	0.0704
	R^2	0.9939	0.9941	0.9960
Freundlich equation	K_F (μmol g^{-1})	3.8175	6.2800	5.8851
	n	1.4180	3.0964	2.8182
	R^2	0.9138	0.9527	0.9145

2.7 Factors affecting adsorption of dye

Few factors affecting adsorption of dye such the contact time, initial dye concentration and amount of adsorbent.

2.7.1 Effect of contact time

Sumari et.al (2009) reported that rapid uptake was observed and gradually reduced with time as equilibrium was reached. At the beginning of contact time, the removal of dye occurred at high rate due to greater available sites for adsorption. However, the active sites became less accesible and eventually saturated as time progressed. It is also reported by Chen et.al (2015) where the adsorption was very fast at the beginning of adsorption process due to high vacant active sites of adsorbent, and reaching a flat plateau after saturation. Pooresmaeil and Namazi (2021) states that the reasons for fast adsorption of amoxicillin (AMX) in the initial time are due to the reduction of the active adsorption sites availability and lower gradient in its concentration. Figure 2.4 shows the removal of AMX from the aqueous solution with time dependent under ambient conditions, dye concentration of 50 ppm, pH 8 and adsorbent dosage of 50 mg.

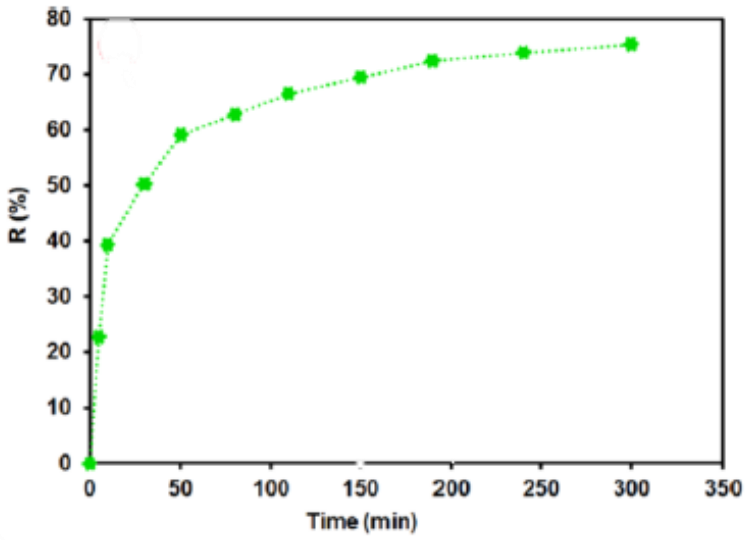

Figure 2.4 Removal dye vs time (Pooresmaeil and Namazi (2021)

2.7.2 Effect of dye concentration

Another parameter to be manipulated is the concentration of dye. The adsorption of methylene blue dye increased with the increasing initial concentration of dye. Based on Zango et.al (2021), the adsorption capacity increased for dye adsorption onto UiO-66 was observed when the initial concentrations were increased from 10 to 100 mg L^{-1}. As reported by Nadiye-Tabbiruka et.al (2018), longer time was needed for concentrated dye solution to reach final equilibrium compared to lower concentrated solutions and having thought that the initial adsorption at higher concentration of dye leads to swelling of the adsorbent, thus exposing the inner surface and pores for more adsorption. As the concentrations dye increased, the higher uptake of the dye was credited to the abundant adsorption site of the MOF as shown by the BET surface area of 247 m^2 g^{-1} (Zango et.al., 2021).

2.7.3 Effect of adsorbent amount

Elaigwu et.al (2010) observed that increasing the adsorbent amount also increases the amount of metal adsorbed on the surface of adsorbent due to decreasing competition for bonding sites between adsorbate. Increasing dosage of Nitrogen-doped Porous Carbon (NPC) has increased the removal efficiency due to the availability of adsorption site, but reduced its adsorption capacity due as the adsorption sites remain unsaturated (Chen et.al., 2018) and the efficiency of colour removal is high as the increasing amount of adsorbent increased the active sites (Adar et.al., 2020). Besides, it might be happened because the adsorbate become the limiting reactant in those reaction. The dye adsorption capacities at different amount of adsorbent can be observed from Figure 2.5, the experimental data conducted by Oguz et.al (2006). The experiment was conducted by changing the powder activated carbon (PAC) dosage

from 1 to 4 g/250 ml and initial Bomaplex Red Cr-L dye concentration was 1000 ppm. It is clear that the equilibrium concentration of Bomaplex Red CR-L dye diminishes with the increasing the PAC dosage for a given initial dye concentration. The authors state that the efficiency of the dye removal was 99% at 30 min of adsorption.

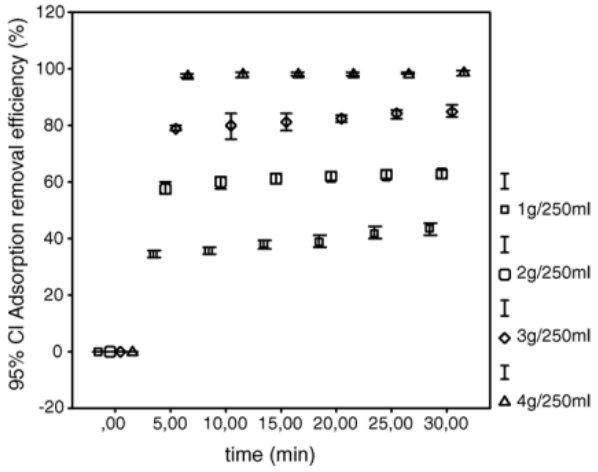

Figure 2.5 Effect of adsorbent concentration on the dye removal efficiency (C_0 1000 ppm, pH 9.3, T 219K, agitation rate 300 rpm) (Oguz et.al., 2006)

2.8 Characterization

It is also important to analyse the characterization of samples of adsorption in order to know its properties. Based on Đolić et.al (2021), a goethite impregnated sample which is fly ash goethite (FAG) was synthesized and optimized using the segment precipitation method, then, it is characterized thoroughly, structurally and morphologically by using liquid nitrogen porosimetry (BET), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Meossbauer spectroscopy (MS) technique.

2.8.1 BET analysis

The synthesized MOF-5 by Greer et.al (2016) recorded a BET surface area of 787.2 m^2 g^{-1} for 30min sample by N_2 sorption, which is lower than expected for simple MOF-5, where all pores are empty. They found the $Zn(OH)_2$ species in the pores that remain upon activation, significantly reducing the pore space and smaller amount of interpenetration. Based on Đolić et.al (2021) studies, the specific surface area for FA and FAG are 8.190 and 26.13m^2g^{-1}, respectively. Significantly higher availability of surface sites were shown after the goethite impregnation, subsequently conceivably adding to an expanded capacity for the FAG's as an adsorbent.

2.8.2 XRD analysis

Greer et.al (2016) carry out XRD test and found out that the crystallinity of metal organic framework – 5 (MOF-5) adsorbent increases with reaction time ranging from 20 min to 3 h. The layered particles that formed during phase transformation of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ to MOF-5 were consumed for longer reaction times (Zheng et.al., 2014). It is determined that as the reaction time increased from 4h to 6h, the amorphous component significantly diminished and was absent in specimens with a reaction time above 10 h. The diffraction pattern from XRD analysis by Naiya et.al (2009) showed the peaks of CaSiO, $CaOFe_2O_3$, $CaOSiO_2$ and some complex phases of $CaO{\cdot}MgO{\cdot}SiO_2$ with Al_2O_3. The XRD analysis for deep eutectic solvents combined with rice husk ash (DES-RHA) sample exhibited wide peaks between 22º and 27º (2θ), which indicated the presence of cristoballite (SiO2) (Kaur et.al., 2021).

2.8.3 SEM analysis

Pooresmaeil and Namazi (2021) carried out the morphology investigation of the fabricated sample by using TESCANMIRA3 scanning electron microscope (SEM), obtaining the SEM images, energy dispersive X-ray (EDX) spectrum and elemental mapping. It is reported that the fabricated chalk like Cd-MOF in the presence of Fe_3O_4 showed a good contact with each other, which means can improve the efficiency of the prepared system as an adsorbent from both porosity and magnetic viewpoints. Fe_3O_4@Cd-MOF@CS has a rough surface of the microspheres, allows the improvement of amoxicillin (AMX) adsorption and leads to higher activity (Pooresmaeil and Namazi, 2021). The surface of the rice husk ash observed by using SEM micrographs showed highly irregular and porous in nature (Naiya et.al., 2009). Meanwhile, the result of adsorbed adsorbent indicates that a greater morphology of RH powder for the adsorption of organic pollutants and metal ions from aqueous solution (Priya et.al., 2022). Another EDX results by Priya et.al (2022) showed the presence of chronium, lead, and zinc ions towards spent RH adsorbent and carbon, magnesium and sulphur for metal ion-adsorbed rice husk powder. While based on the SEM images by Zheng et.al (2014), the large cubic crystal of MOF-5 was produced after a reaction time of 36 h or longer, indicating that the synthesis processes are going well.

2.8.4 FTIR analysis

According to Oguz et.al (2006), the objective of FTIR analysis in the study is the finding whether the colour adsorbed on the powder activated-carbon (PAC) alter the peaks of functional groups on the PAC. Figure 2.6 shows the FTIR spectra of PAC, with specific value of absorbance at different wavenumber while Figure 2.7 shows the

shifting of peaks if functional groups on the PAC after adsorption of Bomaplex Red CR-L dye molecules. The main functional groups of the predicted structure could be observed with relating infrared adsorption peaks (Lin et.al., 2014). Kaur et.al (2021) reported the presence of O-H (3425cm^{-1}), Si-OH (3457 cm^{-1}) and -COOH bond (1739 cm^{-1}) in the prepared deep eutectic solvent – rice husk ash (DES-RHA) adsorbent while Si-O-Si (468 cm^{-1}) and Si-H (794 cm^{-1}) in the prepared RHA adsorbent,

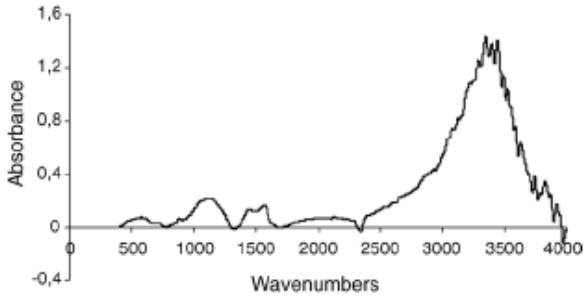

Figure 2.6 FTIR spectra of powder activated carbon (C_0 = 0 ppm) (Oguz et.al., 2006)

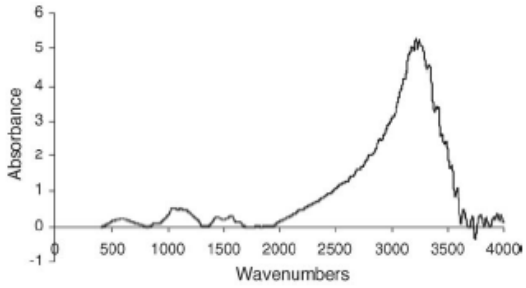

Figure 2.7 FTIR spectra of dyed powder activated carbon (C_0 = 1000 ppm) (Oguz et.al., 2006)

CHAPTER 3

METHODOLOGY

Figure 3.1 is the flowchart of overall process for adsorption decolourization of brilliant green dye study. This project started with the synthesis of modified MOF-5 and followed by the adsorption of brilliant dye. Then, analysis of adsorption, efficiency of dye removal and characterization of modified MOF-5 were conducted in order to have supported data for the report.

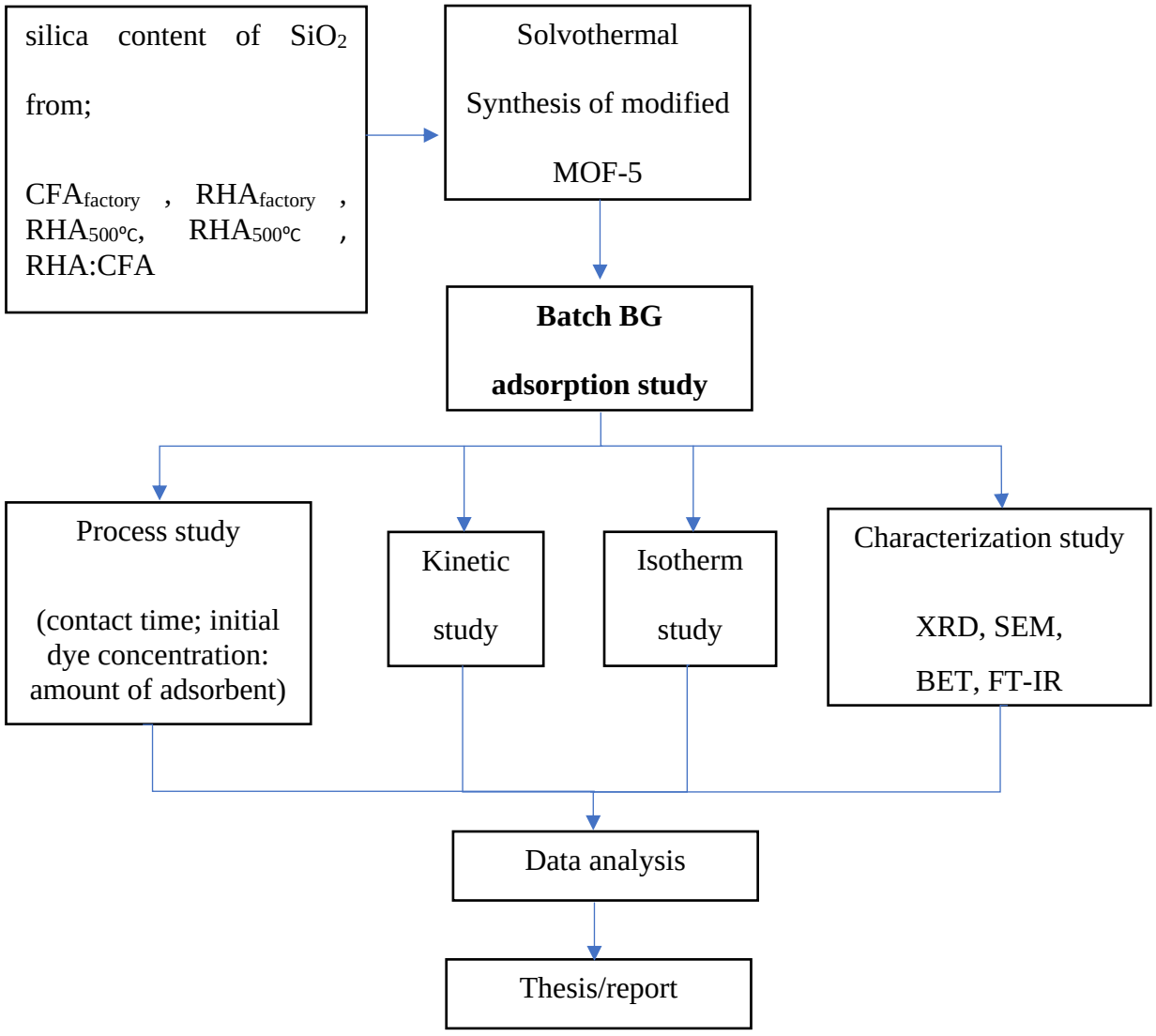

Figure 3.1 Flowchart of overall process