PREPARATION AND CHARACTERIZATION OF IRON OXIDE NANOCOMPOSITE FOR REMOVAL OF METHYLENE BLUE

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by

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LIST OF SYMBOLS

	Symbol	Unit
Ce	Equilibrium concentration of adsorbate	mg/L
Co	Initial concentration of adsorbate	mg/L
Ct	Dye concentration at time, t	mg/L
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Langmuir adsorption constant	L/mg
nf	Constant for Freundlich isotherm	-
qe	Amount of adsorbate adsorbed at equilibrium	mg/g
qm	Adsorption capacity of Langmuir isotherm	mg/g
qt	Amount of adsorbate adsorbed at time, t	mg/g
R^2	Correlation coefficient	-
t	Time	Min
V	Solution volume	L
W	Mass of adsorbent	g
λ	Wavelength	Nm

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
MB	Methylene blue
MO	Metal Oxide
rpm	Rotation per minute
SG	Sol-gel
SS	Solid state
UV	Ultraviolet
XRD	X-ray Diffraction

PENYEDIAAN DAN PENCIRIAN FERUM OKSIDA NANOKOMPOSIT UNTUK PENYINGKIRAN METILENA BIRU

ABSTRAK

Dalam kajian ini, ferum oksida nanokomposit (Fe_2O_3-CuO) telah disediakan dan digunakan sebagai penjerap untuk mengeluarkan metilena biru. Sampel disintesis berdasarkan dua kaedah iaitu kaedah tindak balas keadaan pepejal dan kaedah sol-gel. Dua sampel telah disediakan, iaitu SS02 (‘solid state’) dan SG02 (sol-gel) dan kedua-duanya telah dicirikan berdasarkan kawasan permukaan liang mikro dan jumlah isi padu liang. Bagi sampel SS02, kawasan permukaan liang mikro dan jumlah isi padu liang masing-masing adalah 5.9476 m^2/g dan 0.003061 cm^3/g. Manakala bagi SG02, kawasan permukaan liang mikro dan jumlah isi padu liang adalah 11.0242 m^2/g dan 0.005762 cm^3/g. Komposisi unsur sampel berkenaan telah diperolehi dengan XRD untuk memeriksa kehadiran unsur Fe_2O_3 dan CuO dan ia menunjukkan corak yang hampir sama untuk kedua-dua penjerap yang telah disintesis melalui kaedah yang berbeza. Keberkesanan penjerap ferum oksida nanokomposit terhadap metilena biru dinilai berdasarkan kepekatan awal pewarna (25-300mg / L), masa sentuhan (0-24 jam) dan suhu cecair (30-60ºC). Walaubagaimanapun proses penjerapan yang dicapai terlalu minimun dalam kajian ini kerana ferum oksida nanokomposit didapati tidak sesuai untuk dijadikan penjerap dalam penyingkiran metilena biru.

PREPARATION AND CHARACTERIZATION OF IRON OXIDE NANOCOMPOSITE FOR REMOVAL OF METHYLENE BLUE

ABSTRACT

Iron oxide nanocomposite (Fe_2O_3-CuO) has been prepared and used as an adsorbent in this study to remove methylene blue. The process to synthesize the samples is based on two methods which are solid state reaction and sol-gel method. Two sample prepared, SS02 (solid state) and SG02 (sol-gel) was further characterized and the micropore surface area and total pore volume is determined. For SS02, the micropore surface area and total pore volume are 5.9476 m^2/g and 0.003061 cm^3/g respectively. Meanwhile for SG02, the micropore surface area and total pore volume are 11.0242 m^2/g and 0.005762 cm^3/g respectively. The elemental composition of the samples is obtained by XRD to check the presence of element Fe_2O_3 and CuO and it shows almost identical pattern for both adsorbent that had been synthesized by different method. The effect of initial dye concentration (25-300mg/L), contact time (0-24 hours) and solution temperature (30-60°C) were also evaluated through. However, the adsorption process is not obtained in this study because iron oxide nanocomposite is not suitable for adsorbent in methylene blue removal.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to colour their products. As a result, they generate a considerable amount of coloured wastewater (Crini, 2006). Textile industry involving dye produce large volume of wastewater often rich in colour, containing residues of reactive dyes and chemicals (Gonawala and Mehta, 2014).

Water quality greatly influenced by its colour. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Synthetic dyes are common water pollutants in wastewater and they usually found in trace quantities due to their good solubility (Crini, 2006). Dye effluents that contain complex compound and toxic substances can reduces the oxygen solubility in water, which can affect the aquatic life in downstream environment.

Methylene blue (MB) is one of the most widely applied dyes, often used in dyeing and printing. MB can cause harmful effects such as carcinogenicity, mutagenicity, and toxic effects towards aquatic life (Qi et al., 2015). Additionally, the turbidity levels within discharge streams increases, hindering the ability of fish and other organisms to locate food and reducing photosynthetic activity. For these reasons, treatment of industrial wastewater is of significant concern (Spagnoli et al., 2017).

1.2 Problem statement

Various techniques for the removal of dye from wastewater have been research and applied in the industry. The treatment of dye mainly include physical, chemical and biological method. Such methods include adsorption, ion-exchange, membrane separation, coagulation, chemical oxidation, electrochemical processing, and aerobic and anaerobic microbial degradation. However, achieving the combination of sufficient removal efficiencies, economic viability, and ecological protection is difficult with any of the above processes (Qi et al., 2015).

One of the methods that is found to be more effective, efficient and economic is adsorption process to remove dyes, pigments, and other colorants and also to control the bio-chemical oxygen demand in the wastewater. Many removal techniques have been applied. But, adsorption process is inexpensive and readily available to control the various pollutants from the water and wastewater (Gonawala and Mehta, 2014).

Metal oxide has been used as an adsorbent in removing dye for example, SiO_2, Al_2O_3, Fe_3O_4 and CuO. These metal oxides is a low cost. With nano-particles size, taking advantage of the high specific surface area of nanostructures, metal oxides have been utilized extensively for dye degradation or adsorption purpose. This imparts a considerable change in surface energies and surface morphologies. All these factors are altering the basic properties and the chemical reactivity of nano-materials.

Powdered Fe_2O_3 (Ferric oxide), a brown powder, were recently used in several applications like adsorption, magnetic storage media, solar energy transformation, electronics, Ferro fluids and catalysis. It is used as an effective

adsorbent in the wastewater treatment. The technique was found to be very useful and cost effective for better removal of dye. These particles showed the highest adsorption capacity of removal as compare to other adsorbents (Gonawala and Mehta, 2014).

For CuO, according to Anitha et al., (2014) CuO dose of 30 mg/50 mL was found to achieve ~47% color removal from a wide range of 5 – 40 mg of CuO dose. Therefore, CuO is suitable as an adsorbent for removal of dye.

Based on this information, this work is to study the use of metal oxide nanocomposite Fe_2O_3-CuO in adsorption of methylene blue dye in wastewater.

1.3 Research objectives

The main objectives of this study are:

i. To prepare iron-oxide nanocomposite using conventional solid state reaction and sol-gel method.
ii. To characterize the prepared nanocomposite in terms of surface area, pore volume, pore size distribution and its structure.
iii. To study the effects of adsorbate initial concentration and contact time for adsorption of basic dye on the adsorbents.

1.4 Scope of study

In this work, the Fe_2O_3-CuO nanocomposite adsorbent is prepared via two method, solid state and sol-gel. Calcining temperature is fixed for both method which is 500.

The prepared adsorbent was characterized in terms of surface area, surface morphology, proximate content, elemental content and surface chemistry by using XRD and BET.

Iron oxide nanocomposite were then used for investigation of the adsorption behaviour of MB dye. Batch adsorption study was done to analyse the prepared adsorbent by examined the effect of adsorbate initial concentration (25-300 mg/L) and contact time (0-24 hour) for adsorption of dye onto iron oxide nanocomposite.

CHAPTER TWO

LITERATURE REVIEW

2.1 Dyes

Dyes is a substances that is use to add colour to various substrates including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. There are several types of dye such natural dye, synthetic dye, food dye, and any other dye such leather, laser based on their chemical classification. Some dyes properties can be classified based on their usage as in Table 2.1.

Table 2.1 Classification of dyes and its application (Gupta and Suhas, 2009)

Dyes	**Application**
Acid	Nylon, silk
Cationic (basic)	Paper, polyacrylonitrile
Disperse	Polyester, acrylic fibers
Direct	Cotton, rayon, paper
Reactive	Cotton, cellulosic fiber
Solvent	Plastic, lubricant, gasoline
Sulfur	Cotton, rayon
Vat	Cotton, cellulosic fiber, wool

Dyeing is a process mainly aims at dissolving the dye in water, which will be transferred to the fabric to produce colored fabric under certain conditions. Printing or generally defined as ‘localized dyeing’ i.e. dyeing that is confirmed to a certain portion of the fabric that constitutes the design. For example in textile dyeing and printing process, include pretreatment, dyeing / printing, finishing and other technologies. The main pollutants are organic matters which come from the pre-treatment process of pulp, cotton gum, cellulose, hemicellulose and alkali, as well as

additives and dyes using in dyeing and printing processes. Pre-treatment wastewater accounts for about 45% of the total, and dyeing/printing process wastewater accounts for about 50%~55%, while finishing process produces little (Wang et al., 2011).

The presence of dyes in wastewater is one of the most noticeable indicators of water pollution and the discharge of highly coloured synthetic dye effluents is aesthetically very unpleasing and can damages the receiving water body. These dyes can be toxic, and the biodegradation process is slow and complex, releasing possible carcinogenic products. Their release into the environment creates serious environmental, aesthetical and health problems. Thus, adsorption method is significant in treating dyes in wastewater.

2.2 Adsorption

Process in treating dye in wastewater mainly include physical, chemical and biological treatment process. Each process have their own advantages and disadvantages based on Crini (2006) is summarized in Table 2.2.

Adsorption is the process of accumulating substances that are in solution on a suitable surface. Adsorption process involving four steps, which are bulk solution transport, film diffusion transport, pore transport, and adsorption. It can be classified into two; physisorption and chemisorption. Physisorption or physical adsorption is a type of adsorption when the force of attraction existing between adsorbate and adsorbent are weak Van der Waal forces of attraction. Physical adsorption takes place with formation of multilayer of adsorbate on adsorbent. Meanwhile, chemisorption occurs when the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond. Chemisorption or

chemical adsorption takes place with formation of unilayer of adsorbate on adsorbent.

Table 2.2 Principal existing and emerging processes for dyes removal (Crini, 2006)

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Based on several methods to remove dye in wastewater, adsorption is consider has the advantages of high efficiency, simple design, and low initial costs

compared to other industrial dye removal techniques like coagulation, flocculation, membrane filtration and enzymatic treatment. Adsorption process is inexpensive and readily available to control the various pollutants from the water and wastewater due to its feasibility, simplicity and also involving less economic aspects.

2.3 Metal oxide as adsorbent

Metal oxide (MO) nano-particles have been attracting much attention not only for fundamental scientific research, but also for various practical applications because of their unique physical and chemical properties. Mostly MO have been used specifically for synthesis of many polymer composite, and the specific surface area and adsorption capacity of polymers were improved intensively. Many low cost metal oxides such as SiO_2, Al_2O_3 and Fe_3O_4, which owns abundant of function groups on the surface (Chen et al., 2016). Recent studies also have demonstrated that nanoscale CuO can be used to prepare various organic–inorganic nanocomposites with high thermal conductivity, high electrical conductivity, high mechanical strength, high-temperature durability (Anitha et al., 2014).

Based on Abul et al. (2015) nanocomposite frequently exhibit remarkably improved mechanical and materials properties. For example, CuO is used as an efficient adsorbent for adsorption of MB cationic dye. Copper oxide (CuO) is a p-type semiconductor with an energy band gap of 1.21–1.5 eV due to which it has the capability of performing as a photocatalyst under irradiation of sunlight. Reactions involving Cu^{+}/Cu^{2+} lead to the oxidative transformations of organic compounds. The unique electronic structure of Cu allows the interaction with the spin restricted O_2 enabling Cu to participate in redox reactions with inorganic and organic compounds. CuO finds various applications in current days science and technology, due to its unique features like high specific surface area, chemical stability, electrochemical

activity, high electron communication features, optical switch, pigment, fungicide, metallurgy reagent, gas sensor, magnetic storage media, field emission (FE) emitter, etc (Raizada et al., 2014).

Based on previous study, it proved that Fe_2O_3 is suitable for dye removal. Based on Gonawala and Mehta (2014), the study is carried out on colarane blue BGFS Anthraquinone dye. Powdered Fe_2O_3 has been used for dye removal practical. It was observed that 94% of dye removal efficiency at pH 2 with Fe_2O_3 dosage of 0.3 gm and initial concentration is 125 ppm. Overall, it is found that the prepared Fe_2O_3 powder had high adsorption affinities for anthraquinone blue, which are models of anthraquinone class dyes.

Thus, this work is to study the properties of iron oxide nanocomposite (Fe_2O_3-CuO) as an adsorbent for removal of methylene blue in the wastewater in terms of it chemical composition, porosity, specific surface area and size of particle.

2.4 Adsorption isotherm

The process of adsorption is usually studied through graphs known as adsorption isotherm. Adsorption isotherm is a method used to describe equilibrium relationship between concentration of adsorbate in fluid phase and adsorbent phase at constant temperature. The graph shows the relationship between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. Data is fitted into different isotherm models in order to establish the most appropriate correlations for the equilibrium data in each system. In this research, only two adsorption isotherms namely Langmuir and Freundlich were conducted. Linear regression is used to determine the best-fitting isotherm and the correlation coefficient, R^2 is judged in order to compare the suitability of isotherm equations.

2.4.1 Langmuir isotherm

Langmuir isotherm is the simplest isotherm that widely used for the adsorption of solute from liquid solution. There are few assumptions in this isotherm, which includes:

i. Fixed number of vacant or adsorption sites are available on the surface of solid.

ii. All the vacant sites are of equal size and shape on the surface of adsorbent.

iii. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.

iv. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

v. Adsorption is monolayer or unilayer.

Theoretically, Langmuir model can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.1}$$

then rearranged to get:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{2.2}$$

where,

C_e = Equilibrium concentration of adsorbate (mg/L),

q_e =Amount of adsorbate adsorbed at equilibrium (mg/g),

q_m =Monolayer adsorption capacity of the adsorbent (mg/g),

K_L =Langmuir adsorption constant (L/mg).

Therefore, a graph plot of C_e/q_e against C_e gives a straight line with the slope of $1/q_m$ and intercept of $1/K_Lq_m$. The adsorption coefficient can be determined from the slope and intercept of the straight line.

2.4.2 Freundlich isotherm

Freundlich adsorption equation is an empirical equation. It give accurate description of adsorption of organic adsorption in water. Freundlich-type adsorption is considered to be a multi-layer process in which the amount of adsorbed solute per unit adsorbent mass increases gradually. Theoretically, Freundlich model can be expressed as (Chung et al., 2015):

$$q_e = K_F C_e^{\frac{1}{n_F}} \quad (2.3)$$

which can then be further rearranged to:

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (2.4)$$

where,

q_e = Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),

$1/n_F$ = Adsorption intensity,

C_e = Equilibrium concentration of the adsorbate (mg/L),

K_F = Freundlich isotherm constant (mg/g (L/mg) $^{1/n}$).

Therefore, a graph of ln q_e against ln C_e gives a straight line with the slope of $1/n_F$ and intercept of ln K_F. From the slope of graph, the value of $1/n_F$ measures the adsorption intensity or surface heterogeneity. When the value of adsorption intensity is close to 0, it indicates that the system become more heterogeneous. Meanwhile, with the value lower than 1, it shows a normal Langmuir isotherm. Meanwhile, if the value above 1, it shows that the system is from cooperative adsorption (Fytianos et

al., 2000). Additionally, from the intercept of graph, the value of K_F can be determined. Generally, K_F is a constant related to the bonding energy of a system. It is the adsorption or distribution coefficient that represents the quantity of dye adsorbed onto adsorbents for a unit equilibrium concentration.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Fe_2O_3-CuO nanocomposite was prepared from Iron (III) Nitrate Nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and Copper Nitrate ($Cu(NO_3)_2$). The molecular weight for both chemicals are 404.00 g/mol and 241.60 g/mol respectively. R and M Chemicals supplied these chemicals. Methylene blue (MB) used as adsorbate was supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia. Ethanol was used as solvent during preparation of Fe_2O_3-CuO nanocomposite to mix the component in both method.

3.2 Equipment and instrumentations

3.2.1 Preparation of Fe_2O_3-CuO nanocomposite adsorbent

List of equipment used is listed in Table 3.1

Table 3.1 List of equipment

Equipment used	**Model**
Electronic balance	Shimadzu Corporation
Mortar	
Muffle furnace	Carbolite
Hot plate stirrer	IKA RET basic
Oven	Memmert

3.2.2 Characterization of prepared adsorbent

All the samples prepared were characterized using XRD and BET prior to adsorption process. The crystallography and element in the composition was determined by using X-Ray Diffraction (XRD) (Model Bruker). The specific surface area, porosity and also particle size of the adsorbent form was determined by BET analyser (Micromeritics ASAP 2020 volumetric adsorption analyser).

3.2.3 Dye concentration

In order to determined the concentration of the dye in the solution, a double-beam UV-Visible spectrometer (Thermo Scientific Genesys 20) was used. The wavelength of MB was set at 663 nm.

3.2.4 Adsorption test

The adsorption tests was performed by preparing a set of Erlenmeyer flasks (250 ml) filled with 0.20 g of the prepared Fe_2O_3-CuO nanocomposite adsorbent and 200 ml of prepared dye solutions. Six different dye concentrations of 25, 50, 100, 200, 250 and 300 mg/L were prepared by mixing a known amount of dye with deionized water. After that, the Erlenmeyer flasks were sealed and placed in water bath shaker at a speed of 60 rpm and maintain at temperature of 30^{o}C for 24 hours.

3.3 Experimental procedures

The overall experimental activities carried out in this study are presented in the following schematic flow diagram:

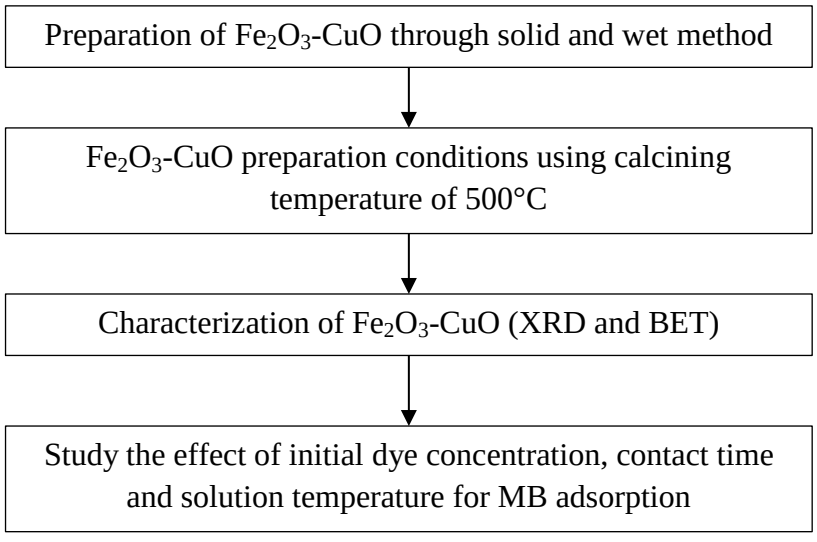

Figure 3.1 Overall experiment activities

3.3.1 Preparation of Fe_2O_3-CuO

Two samples of iron oxide nanocomposite adsorbent was prepared by different method. SS02 and SG02 refer to solid state and sol-gel method respectively.

a) Solid state method, SS02

Fe_2O_3-CuO adsorbent was prepared by reaction of 1:1 ratio between Fe_2O_3 and CuO. In this study, chemical used was Iron (III) Nitrate Nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and Copper Nitrate ($Cu(NO_3)_2$).

The chemicals were weight to desired amount and mix with a few drop of ethanol as solvent. The sample prepared was then grinded using mortar to get a viscous solution. The sample was heated in the furnace up to 500°C. The temperature is dwell up to 3 hours. After the heating process, the sample were in solid form.

b) Sol-gel method, SG02

The initial preparation was the same with the solid state method, whereas the chemicals were weight at same amount and mix together with 50 ml of ethanol as solvent. It would form viscous solution. The sample was prepared in Erlenmeyer flask and being reflux for 10 minutes at 75°C. Then, the sample was put in the oven at 80°C for 24 hours. After that, the powder formed was crushed with mortar and stored in the furnace at calcining temperature of 500°C.

3.3.2 Preparation of MB dye

Methylene blue dye was prepared by dissolving 1 g of MB dye powder in 1000 ml of deionized water to get 1000 mg/L solution for adsorption test. Dilution of the prepared solution within the range from 25 to 300 mg/L were then prepared by using deionized water.

3.3.3 Sample analysis

Sample analysis meant to study the adsorption activity of MB using as-prepared Fe_2O_3-CuO. The sample was collected at every time interval to see the concentration of the dyes in the solution. The respective dye concentration was determined by using UV-visible spectrometer. For MB dye, the wavelength was set at 663 nm. The linear relationship between absorbance of the dyes onto iron oxide nanocomposite and concentration was plotted in graph of absorbance versus concentration of the dye solutions.

3.3.4 Adsorption test

The adsorption tests were conducted to study the adsorption performance of the prepared Fe_2O_3-CuO adsorbent in removing MB dye in the solution 0.20 g Iron Oxide nanocomposite adsorbent was added into a series of Erlenmeyer flask filled with 200 ml of dye solutions with different initial concentrations within the range 25-300 mg/L. The Erlenmeyer flasks were then sealed and placed in the isothermal water bath shaker at 30^{o}C with agitation speed of 60 rpm. For a certain time interval, the aqueous samples were taken and the concentrations were measured using UV-Vis spectrometer based on the wavelength of maximum adsorption. These measurement steps were repeated until a steady state was reached. For equilibrium studies, the amount of adsorption at equilibrium, q_e can be determined by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{3.3}$$

where, C_o = Liquid-phase dye concentrations at initial stage (mg/L),

C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L),

V = Volume of dye solution (L),

W = Mass of adsorbent used (g).

Meanwhile, the percentage of dye removal, % *C* can be calculated by using:

$$\% C = \frac{(C_o - C_t)}{C_o} \times 100 \quad (3.4)$$

where C_t is liquid-phase dye concentrations at time.

Langmuir and Freundlich were used to fit the experimental data. The best-fitted isotherm can be determined through the value of correlation coefficient; R^2 which is closest to the unity. Meanwhile, the amount of adsorption at time *t*, q_t (mg/g), was calculated by using:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (3.5)$$

where,

C_o = Liquid-phase dye concentrations at initial stage (mg/L),

C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L),

V = Volume of dye solution (L),

W = Mass of adsorbent used (g).

3.3.5 Effect of initial dye concentration and contact time

In order to investigate the effect of initial dye concentration and contact time on the adsorption uptake, the adsorption temperature of solution was kept constant at 30^{o}C. 200 ml of respective dye solutions with initial concentration of 25 to 300 mg/L were prepared in a series of 250 ml Erlenmeyer flasks and 0.20 g of adsorbent prepared was added into each flask. The solutions were then shaking in the water bath shaker at 30^{o}C with agitation speed of 60 rpm until the equilibrium stage is reached.

3.3.6 Effect of solution temperature

Similar procedure was then carried out at 3 different solution temperatures, 30, 45 and 60 ºC under constant initial dye concentration of 25 mg/L. Same dosage of adsorbent, volume of dye solution and speed of rotation were utilized.

CHAPTER FOUR

RESULT AND DISCUSSION

In this chapter, data and results from the conducted experiment is presented and discussed. The part of discussion consist of the characterization of the samples and batch adsorption studies of the nanocomposite metal oxide (Fe_2O_3-CuO) for methylene blue (MB) adsorption.

4.1 Characterization of nanocomposite Fe_2O_3-CuO

The samples were characterized in terms of surface area, pore volume, pore size distribution, surface morphology, and elemental composition.

4.1.1 Surface area and pore characteristics

The analysis of surface area and pore characteristics for the samples are shown in Table 4.1. Based on micropore surface area, SG02 has higher surface area compared to SS02. This factor influenced the adsorption process later where the higher surface area will improve for adsorption process to take place.

Table 4.1 Surface area and pore characteristics of the samples

	BET surface area (m^2/g)	**Micropore surface area (m^2/g)**	**Total pore volume (cm^3/g)**
SS02	6.3186	5.9476	0.003061
SG02	1.4316	11.0242	0.005762

4.1.2 Characterization by XRD

Figure 4.1 below shows the XRD pattern of Fe_2O_3-CuO composition of the nanocomposite metal oxide prepared using solid-state and sol-gel method. Both spectrum shows almost identical pattern for both adsorbent that had been synthesized by different method. These patterns identical to the work done by Khedr et al. (2014) who report on XRD of CuO-Fe_2O_3. Therefore, the pattern showed the correct composition present in the sample. For sample SS02, which refer to solid state method, an amorphous structure is obtained. Number 1 and 2 in the figure represent Fe_2O_3 and CuO respectively. There are impurities in SG02 sample may due to contamination during preparation of the sample.

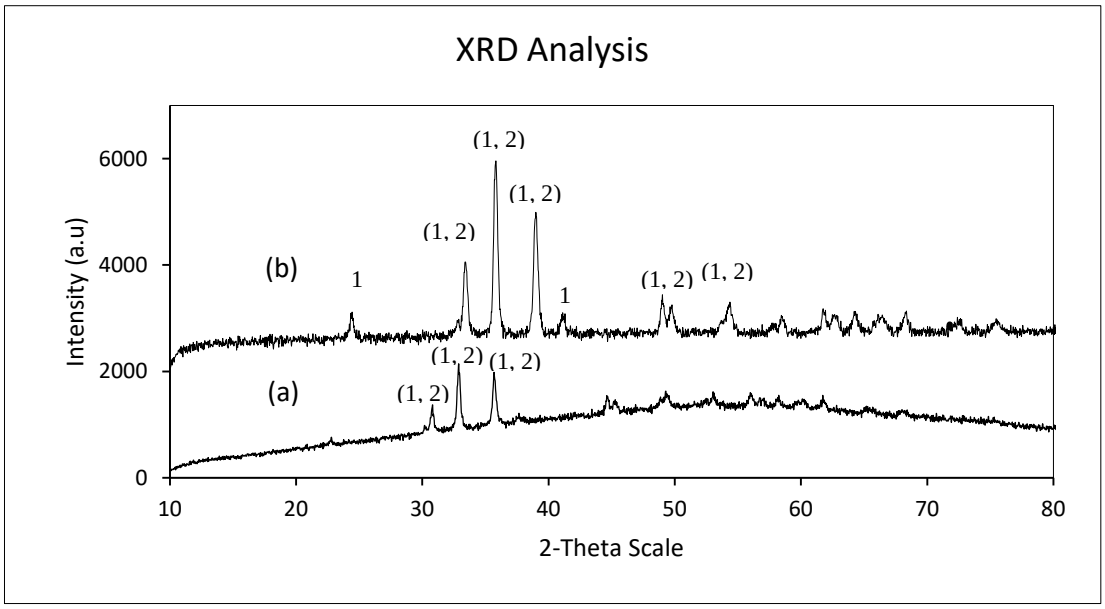

Figure 4.1 XRD pattern of Fe_2O_3-CuO for (a) SS02 and (b) SG02 samples

4.2 Batch adsorption studies of MB on samples

The metal oxide nanocomposite adsorbent, Fe_2O_3-CuO was tested in order to assess the feasibility as adsorbent. The study was conducted based on the effect of initial dye concentration, contact time and solution temperature.

4.2.1 Effect of initial dye concentration and contact time

The results show the effect of contact time of the adsorbent with the dye solution within 24 hours at various initial dye concentration range from 25-300 mg/L at 30°C. Based on Figure 4.2 and 4.3, the result shows the removal percentage and adsorption uptake of MB by SS02 shows a positive value only for 25 mg/L of initial dye concentration. The removal takes place in the adsorption process around 10-20%. For dye concentration of 50-300 mg/L, the results show that no adsorption reaction takes place thus indicate no adsorption process takes place in SS02 adsorbent.

From Figure 4.4 and 4.5, the removal percentage and adsorption uptake for SG02 as adsorbent is displayed. Based on the results, for initial dye concentration of 25 and 50 mg/L, percentage of removal between 10-30% takes place. The removal of the MB does not show a consistent trend. For 100-300 mg/L, the results show negative values, as there are no reaction of adsorption occurred.

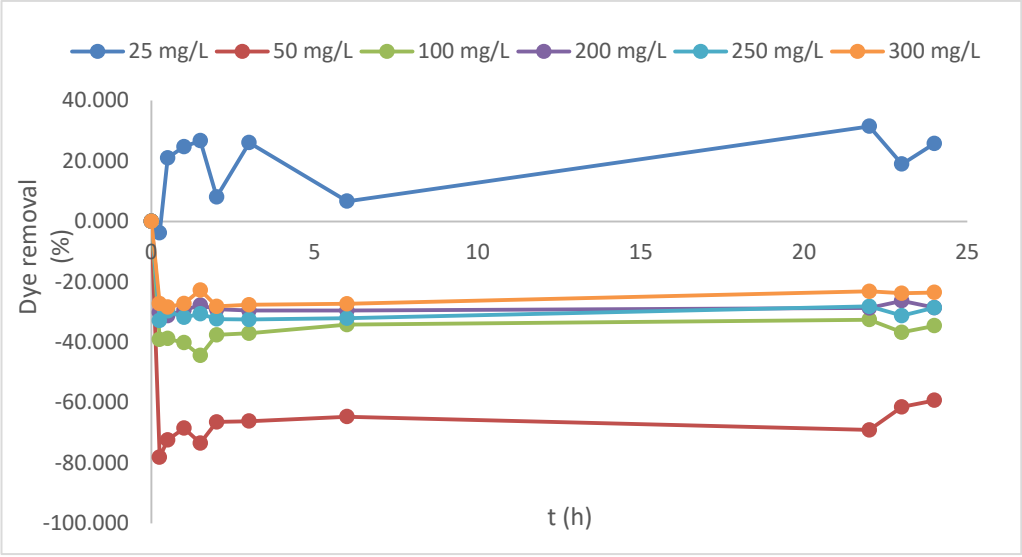

Figure 4.2 Percentage of removal by SS02

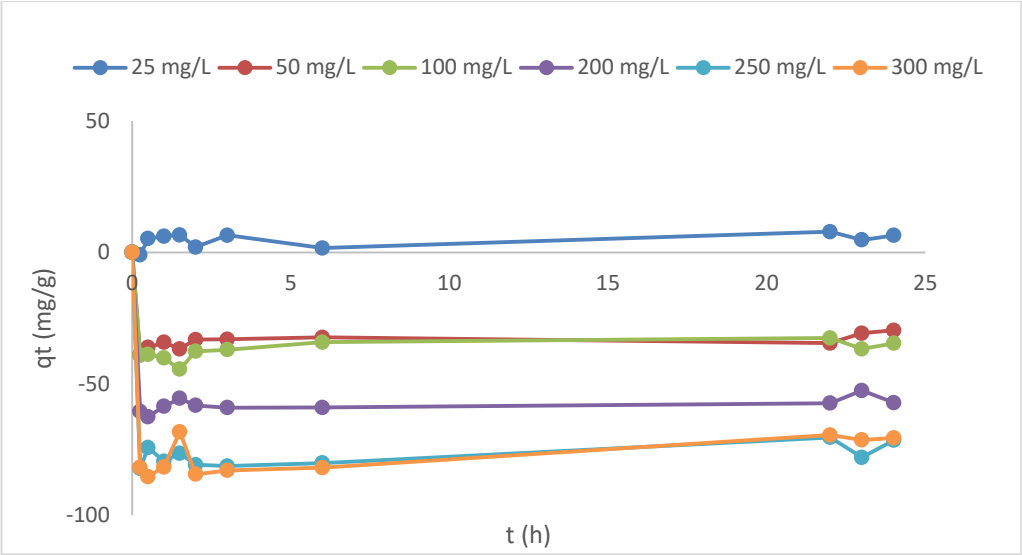

Figure 4.3 Dye adsorption uptakes versus adsorption time at various initial dyes concentrations at 30^0C for MB by SS02

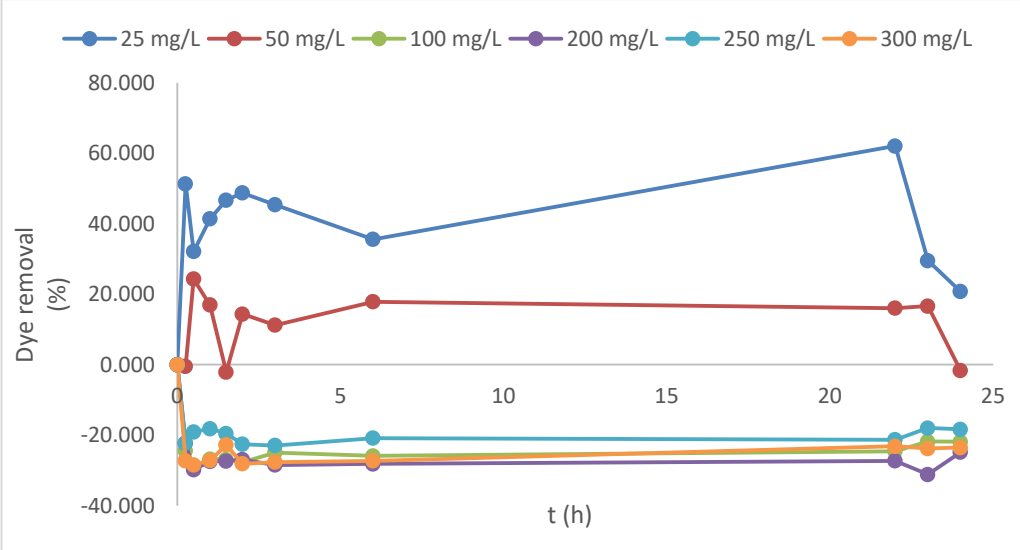

Figure 4.4 Percentage of removal by SG02

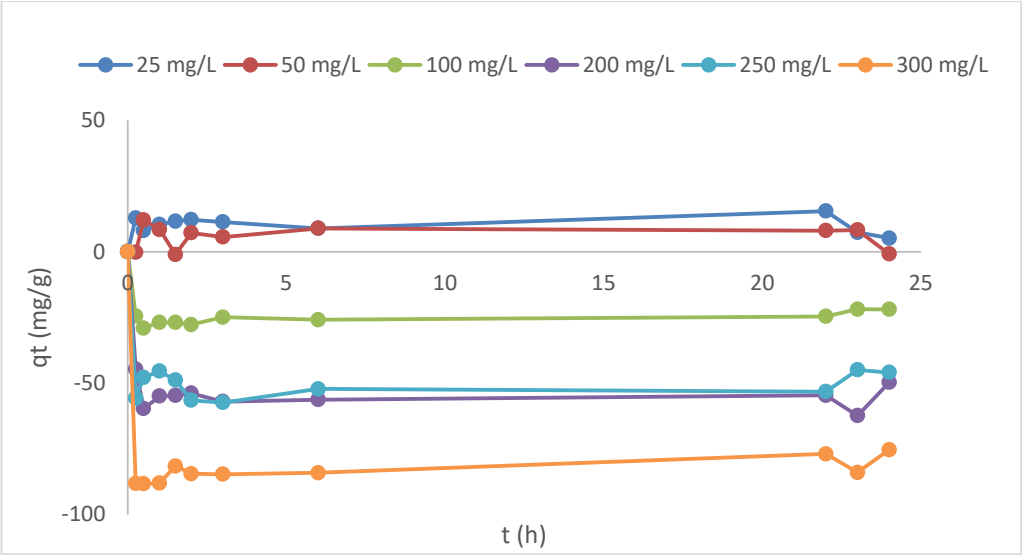

Figure 4.5 Dye adsorption uptakes versus adsorption time at various initial dyes concentrations at 30^0C for MB by SG02

Higher percentage removal of SG02 compared to SS02 is related with the structure of the samples. Very minimum amount of adsorption uptake that occur was due to the vacant sites and porosity of the adsorbent. Based on the analysis and characterization before, it shows that SG02 has higher surface area and pore volume than SS02. The higher the surface area and porosity of SG02 compared to SS02 allows adsorption to occur but in a small amount. It is because, its pore volume only have 0.005762 cm^3/g, which is considered too small for adsorption process. Based on Păcurariu et al. (2016), the minimum pore volume for MB removal to occur is 0.23 cm^3/g that give 99.69% removal.

Thus, these results can be attributed to the low availability of adsorption sites of the sample to remove the MB in the solution. For very low concentration, it is possible for adsorption to take place as minimum dye molecule presence in the solution can easily attach on the external surface of adsorbent, allow a small reaction of adsorption process to occur.

4.2.2 Effect of solution temperature

One of the parameter that need to be consider in an adsorption process is the temperature. As shown in Figure 4.6 and 4.7, three different temperatures (30, 45 and 60^{0}C) over a range of initial dye concentrations were studied. As very little removal of MB is takes place in the adsorption process, the negative results is obtain throughout the temperature variation.

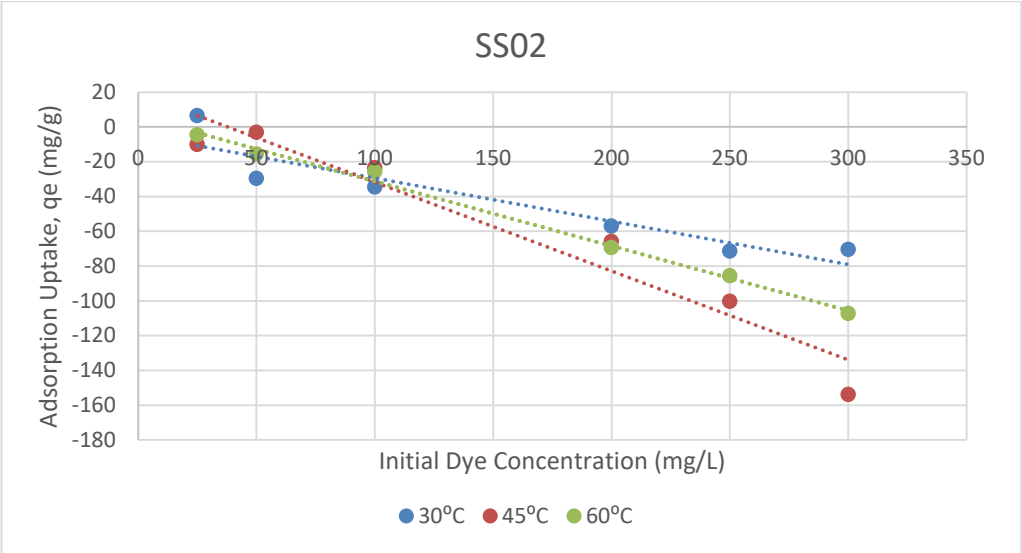

Figure 4.6 Dyes adsorption uptake versus initial dye concentration at different temperatures for MB by SS02

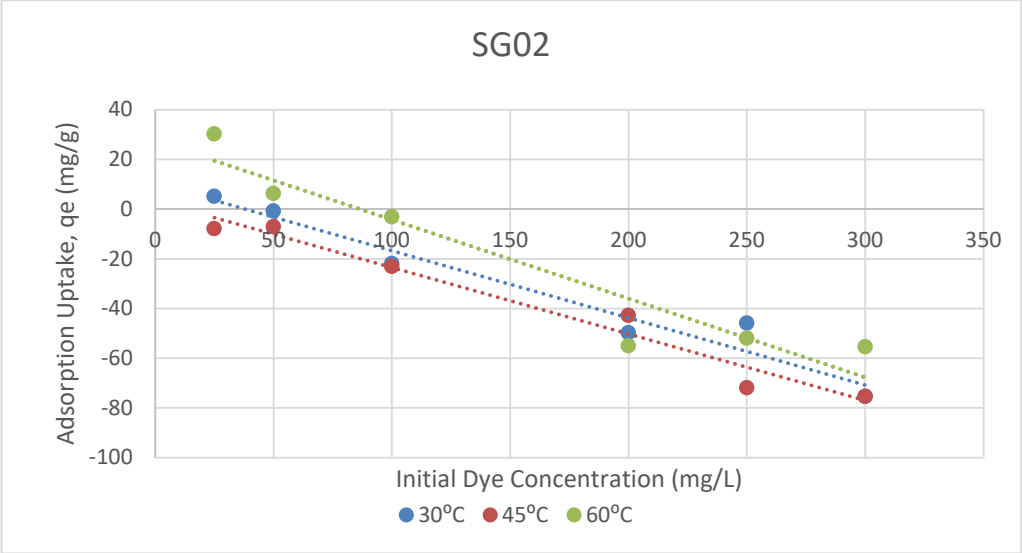

Figure 4.7 Dyes adsorption uptake versus initial dye concentration at different temperatures for MB by SG02