

SYNTHESIS OF CARBON NANOTUBES - MESOSTRUCTURED SILICA
NANOPARTICLES COMPOSITES FOR ADSORPTION OF METHYLENE BLUE

AINUL HAKIMAH KARIM

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Universiti Teknologi Malaysia

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ABSTRACT

The mesostructured silica nanoparticles (MSN) have been widely developed for the removal of various pollutants due to their highly porous structure and other novel features. While carbon nanotubes (CNT) are attracting great interest owing to its large specific surface area, small size, hollow and layered structures. The integration of these outstanding properties by modification of MSN with singlewalled CNT (SWCNT) and multiwalled CNT (MWCNT) is quite new in this area of study and is expected to produce an adsorbent with higher adsorption capacity. In this study, three types of adsorbents were prepared by a simple one step method; MSN, series of SWCNT-MSN composites, and series of MWCNT-MSN composites. Their characteristics have been observed by XRD, N₂ physisorption, FTIR, TEM, and FESEM, while their adsorption performance were evaluated on the adsorption of methylene blue (MB) at various pH, adsorbent dosage, initial MB concentration, and temperature. The results demonstrated that the adsorbents were prepared with mesoporous structures and produces relatively higher number of pores with larger diameters. The CNTs were found to improve the physicochemical properties of the MSN and led to an enhanced adsorptivity for MB. N₂ physisorption measurements revealed the development of a bimodal pore structure in MWCNT-MSN composites that increased the pore size, pore volume and surface area. The best conditions for MSN, SWCNT-MSN and MWCNT-MSN composites achieved at pH 7 and 303 K using 0.05 g L⁻¹ adsorbent and 100 mg L⁻¹ MB. Fitting with linear Langmuir isotherm produce the maximum adsorption capacity of 500.1 mg g⁻¹, 500.0 mg g⁻¹, and 263.2 mg g⁻¹ for MSN_{AP}, SWCNT-MSN and MWCNT-MSN, respectively. The equilibrium data were evaluated using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models, with the Freundlich model affording the best fit to the adsorption data for MSN and Langmuir model for both SWCNT-MSN and MWCNT-MSN. The adsorption kinetics for all MSN, SWCNT-MSN and MWCNT-MSN were best described by the pseudo-second order model. Thermodynamic study showed that the nature of MSNs and MWCNT-MSNs are exothermic, and endothermic for SWCNT-MSNs. This study is proven to produce a relatively new and potential mesostructured materials used as adsorbent for dye removal and water treatment.

ABSTRAK

Zarahnano silika mesolintang (MSN) telah dikaji dengan meluas untuk tujuan merawat pelbagai jenis bahan cemar berdasarkan ketinggian struktur berliangnya dan ciri-ciri istimewa lain yang dimilikinya. Manakala karbon bertiub-nano (CNT) telah menarik perhatian ramai penyelidik kerana luas permukaan yang tinggi, saiz yang kecil, serta struktur yang berongga dan berlapis. Integrasi sifat-sifat pada dua bahan ini menerusi modifikasi antara MSN, dan dua jenis CNT iaitu CNT dinding tunggal (SWCNT) dan CNT multi-dinding (MWCNT) merupakan kajian yang baru dalam bidang ini dan dijangka menghasilkan penjerap dengan keupayaan penjerapan yang tinggi. Dalam kajian ini, tiga jenis penjerap telah disintesis menggunakan satu kaedah yang ringkas; iaitu MSN, siri komposit SWCNT-MSN, dan siri komposit MWCNT-MSN. Sifat-sifat penjerap telah dicirikan menggunakan XRD, N_2 physisorption, FTIR, TEM dan FESEM, manakala prestasi penjerapan mereka telah dinilai keatas metilena biru (MB) pada pelbagai pH, dos penjerap, kepekatan MB awal, dan suhu. Keputusan menunjukkan penjerap memiliki struktur berliang dan bilangan liang yang tinggi dengan diameter yang besar. CNT dipercayai telah meningkatkan sifat kimia-fizik MSN seterusnya menggalakkan penjerapan terhadap MB. Pengukuran dengan N_2 mendedahkan penghasilan struktur liang bimodal dalam komposit MWCNT-MSN yang menambah saiz dan isipadu liang, serta luas permukaan. Keadaan terbaik untuk ketiga-tiga jenis penjerap MSN, SWCNT-MSN dan MWCNT-MSN telah dicapai pada pH 7, bersuhu 303 K menggunakan 0.05 g L^{-1} penjerap dan kepekatan awal MB 100 mg L^{-1} . Keupayaan penjerapan maksimum Langmuir untuk MSN_{AP} , MWCNT-MSN dan SWCNT-MSN masing-masing adalah 500.1 mg g^{-1} , 500 mg g^{-1} , dan 263.2 mg g^{-1} . Data keseimbangan telah ditaksir dengan model isotherm Langmuir, Freundlich, Temkin, dan Dubinin-Radushkevich, dengan model Freundlich paling sesuai untuk MSN dan model Langmuir paling sesuai untuk MWCNT-MSN dan SWCNT-MSN. Kinetik penjerapan untuk kesemua penjerap MSN, SWCNT-MSN dan MWCNT-MSN pula menepati model tertib pseudo-kedua. Kajian termodinamik menunjukkan MSN dan MWCNT-MSN bersifat eksotermik, manakala SWCNT-MSN bersifat endotermik. Dapatan kajian ini membuktikan bahan berstruktur mesolintang yang baru dan berpotensi telah berjaya disediakan dan digunakan sebagai penjerap dalam penyingkiran pewarna dan rawatan air.

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LIST OF ABBREVIATIONS

APTES	-	3-aminopropyl triethoxysilane
BET	-	Brunauer Emmet Teller
BJH	-	Barrett, Joyner, and Halenda
CNT	-	Carbon Nanotubes
CTAB	-	Cetyl Trimethyl Ammonium Bromide
FESEM	-	Field Emission Scanning Electron Field
FTIR	-	Fourier Transform Infra-Red
MB	-	Methylene Blue
MCM-41	-	Mobil Compound Mesoporous – 41
MSN	-	Mesostructured Silica Nanoparticles
MSN _{AP}	-	Mesostructured Silica Nanoparticles prepared with APTES
MSN _{UN}	-	Mesostructured Silica Nanoparticles prepared without APTES
MWCNT	-	Multiwalled CNT
SBA-15	-	Santa Barbara Amorphous -15
SWCNT	-	Singlewalled CNT
TEM	-	Transmission Electron Field
TEOS	-	Tetra Ethyl Ortho Silicate
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

C_i	-	Thickness of the boundary layer
C_o	-	Initial MB concentration (mg L^{-1})
C_t	-	MB concentration at time t of reaction (mg L^{-1})
C_e	-	MB concentration at equilibrium time (mg L^{-1})
k_1	-	Pseudo-first order rate constant (min^{-1})
k_2	-	Pseudo-second order rate constant ($\text{mg g}^{-1} \text{min}^{-1}$)
k_{id}	-	intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-1/2}$)
K	-	Kelvin
K_L	-	Langmuir constant
K_F	-	Freundlich constant
K_T	-	Temkin constant
K_{DR}	-	Dubunin-Radushkevich constant
m	-	Mass (g)
n_F	-	Heterogeneity factor
q_e	-	Adsorption uptake at equilibrium conditions (mg g^{-1})
q_t	-	Adsorption uptake at time t (mg g^{-1})
q_m	-	Maximum adsorption capacity (mg g^{-1})
R	-	Gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	-	Absolute temperature (K)
V	-	Volume of solution (L)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The increasing development of wide range of industries was resulted to the discharge of highly coloured and variety of synthetic dye effluents into water stream. Moreover, the large-scale production of synthetic dyes which are potentially toxic to living organisms and even carcinogenic to humans and aquatic life is of great environmental concerns (NIOSH, 1980; Moreira, 2004).

In order to solve this environmental issue, various treatment methods have been studied, developed, and reviewed to remove dyes and other pollutants from wastewater. Some of them are flocculation, sedimentations, flotation, filtration, membrane separations, ion-exchange, oxidation and adsorption. Among them, adsorption process has been established as an effective and simple approach to remove dye from wastewater. For this purpose, activated carbons have become one of the most widely used adsorbents. However, these materials suffer from some drawbacks, such as costly regenerations, non-selective uptake as well as the adsorption capacity requires other types of materials to be proposed, developed and evaluated to meet this need (Walcarius and Mercier, 2010).

With increasing environmental concerns worldwide, nanoporous materials have given attention for the separation of polluting species and the recovery of useful ones. Environmentally and friendly zeolites were studied extensively. The reason for their success is related to their specific features in converting molecules

having kinetic diameter below 1 nm, but they become insufficient when reactants with sizes larger than the pores is targeted. Research efforts to synthesize materials with larger pore diameter, high structural stability and adsorptive activity in extending the applications of zeolites come with a new material namely mesoporous or mesostructured silica nanoparticles.

Mesostructured silica nanoparticles have been well developed in these two decades since the discovery by Mobil researchers (Kresge *et al.*, 1992), Kuroda and his co-workers (Yanagisawa *et al.*, 1990), and (Inagaki *et al.*, 1993). This material, with large pore diameters ranging from 2 to 50 nm have been a focus of many researches because of their high specific surface areas, controllable structures and compositions, which make them suitable for a wide range of applications in catalysis, adsorption, separation, chromatography, etc. The pore size of mesoporous silica is large enough to accommodate a variety of large and bulky molecules, and the high density of silanol groups on the pore wall is beneficial to the introduction of functional groups with a high coverage.

Various kinds of surface modifications have been conducted for providing new functions for the surfaces of mesostructured in order of making them suitable for a wide range of applications such as in catalysis, adsorption, separation, and chromatography.

Carbon nanotubes (CNTs) have attracted great attention in nanoscale science and technology due to their unique optical, electronic and mechanical properties (Popov, 2004; Smart *et al.*, 2006; Wu *et al.*, 2009; Eder, 2010). They are an attractive alternative for the removal of organic and inorganic contaminants from water, because they have a large specific surface area, small size, hollow and layered structures. Furthermore, the wide range of unique features of CNTs specifically in their adsorption properties are resulted from their hollow, layered nanosized structures (Rodríguez *et al.*, 2010; Yao *et al.*, 2010b), and strong van der Waals binding energy for molecular adsorbates on adsorption sites (Ren *et al.*, 2011). Recently, CNTs have been found to be efficient adsorbents with a capacity that exceeds that of activated carbon (Long and Yang, 2001; Lu and Chiu, 2006).

However, the formation of CNT aggregates limits the ability of CNTs to disperse homogeneously in various solvents and also causes difficulties in the separation process (Wang *et al.*, 2010). Considering the potential use of CNTs in wastewater treatment, numerous studies have been done on their hybridization with other materials such as chitosan (Chatterjee *et al.*, 2010), activated carbon fiber (Wang *et al.*, 2010), graphene (Ai and Jiang, 2012), and cellulose (Deng *et al.*, 2012) in order to enhance their dispersion properties and adsorption capacities.

Several efforts have been also made to hybridize CNTs with other well-performing materials. For instance, alumina coated onto CNT improved their ability to remove Pb(II) and Ni(II) ions (Amais *et al.*, 2007) as compared to the parent, while mesoporous TiO₂-CNT composites improved the photodegradation of the air pollutant acetone (Yu *et al.*, 2005). In addition, CNTs have also been hybridized with mesoporous silica materials such as SBA-15 (Vila *et al.*, 2009) and MCM-41 (Wang *et al.*, 2009) in which the physical properties of the composites were reported have been improved.

However, as the best to our knowledge, detailed studies on the effect of modification with CNTs upon the physicochemical properties of mesostructured silica nanoparticles (MSN) as well as their subsequent application to dye adsorption is still rare. Therefore, in this study we report on a preparation of MSN loaded with different percentages of multiwalled CNTs (MWCNT) and singlewalled CNT (SWCNT) to produce a series of CNT-MSN composites. The synthesized CNT-MSN composites were then characterized by X-ray diffraction, Fourier transform infrared spectroscopy, nitrogen physisorption, and transmission electron microscopy. We found that the physicochemical properties of the composite were improved in term of the interaction between adsorbents, and thus enhanced their adsorption capability towards MB dye. The adsorption equilibrium, kinetics and thermodynamics of the adsorption were also investigated.

1.2 Problem Statement and Hypothesis

Discharge of methylene blue dye effluents from industrial area into water stream may cause serious environmental effects especially to aquatic life and their consumers, due to their toxicity, harmful, and carcinogenic effect. Moreover, solubility and stability of methylene blue in water made this kind of dye difficult to be removed by conventional methods. Therefore, finding and developing the most practical method and material for this purpose is beneficial.

To date, adsorption has been established for the simple, easy and effective approach in removal technology. For this purpose, activated carbons have become one of the most widely used adsorbents. However, these materials suffer from some disadvantages, such as costly regenerations, non-selective uptake. Hence, the adsorption capacity requires other types of materials to be proposed, developed and evaluated to overcome these disadvantages (Gong *et al.*, 2009; Walcarius and Mercier, 2010; Ren *et al.*, 2011).

Mesostructured silica nanoparticles adsorbent with outstanding features has been explored for the removal of various pollutants (Walcarius and Mercier, 2010). This material becomes great interest due to their high specific surface area, high thermal and mechanical stability, and highly uniform pore distribution. These outstanding features make it an excellent adsorbent with high adsorption capacity. However, adsorption of methylene blue needs adsorbent with ultimately high surface area and high interaction in such way to improve the efficiency of adsorption. Therefore, modification of MSN with carbon nanotubes (CNTs) was studied.

Carbon nanotubes (CNTs) have attracted great attention in nanoscale science and technology due to their unique optical, electronic and mechanical properties, also good adsorption capacities due to their hollow, layered nanosized structures. However, the formation of CNT aggregates limits the ability of CNTs to disperse homogeneously in various solvents and also causes difficulties in the separation process

The modification of MSN with carbon nanotubes (CNT-MSN) was quite new in this area of study. They have not been explored extensively to remove dye via adsorption. It is expected to enhance adsorption activity in term of the adsorption capacity, rate of adsorption, and its selectivity towards wide range of pollutants. The integration of the superior feature of mesostructured silica nanoparticles and carbon nanotubes were estimated to generate a competent material as adsorbents. The combination structure of both materials is expected to improve the physical properties of CNT or MSN alone (high surface area and pore amount) and subsequently may increase the physical interaction which may led to high adsorption capacity towards methylene blue dye. Besides, the structure of CNT with high π - π interaction may attract the MB molecules at the benzene ring structure (Li *et al.*, 2014).

1.3 Objectives of Study

The objectives of this study are:

1. To synthesize mesostructured silica nanoparticles (MSN) and modified MSN with carbon nanotubes (CNT-MSN) adsorbent.
2. To characterize MSN and CNT-MSN adsorbents.
3. To determine the performance of adsorbents towards the adsorption of methylene blue.
4. To determine the equilibrium isotherm, kinetics, and thermodynamics of MSN and CNT-MSN adsorbents.

1.4 Scope of Study

This study comprises some components in order to complete the objectives outlined in this study. Typically, mesostructured silica nanoparticles (MSN) were synthesized from cetyltrimethylammonium bromide (CTAB) as structure-directing

agent or template, TEOS as silica source and ammonia solution by sol-gel method. The synthesis takes place at 323 K. Next, the obtained sol-gel was aged, centrifuged, washed, dried and calcined at 823 K.

A part of this study involves synthesis of MSN with an addition of 3-aminopropyl triethoxysilane (APTES) as pore expander. The APTES was introduced to the MSN by co-condensation method. Another part of this study is modification of MSN with CNT. Two types of CNT was used, they are MWCNT and SWCNT.

The prepared MSNs and CNT-MSNs composites were characterized by XRD, N₂ physisorption, FTIR, TEM, and FESEM to establish their physicochemical-properties in term of mesostructured phase and crystallinity, surface area, pore size distribution, and particle size.

Next, the performances of the adsorbents were executed towards the adsorption of methylene blue in aqueous solution. The adsorption process is carried out in a batch system under varying pH (2-11), adsorbent dosage (0.1-0.5 g L⁻¹), initial MB concentration (5-100 mg L⁻¹), and temperature (303-323 K).

The adsorption mechanism of MB onto adsorbents was studied over equilibrium isotherm, kinetics models and thermodynamic. The four widely used isotherm model were used to study the adsorption behavior, they are Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. Meanwhile, three conventional kinetic models, namely Lagergren pseudo-first order, Ho pseudo-second order, and Weber and Morris Intraparticle diffusion model have been used. Lastly, the adsorption enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) were calculated using the thermodynamic functions.

1.5 Significance of Study

This study was accomplished to prepare mesostructured silica and CNT-MSN composites. The prepared materials were characterized and the adsorptive ability of

the prepared material was studied in details to elucidate the relationship of their physicochemical properties with the performance. The prepared CNT-MSN with larger pore size improved the adsorptive sites and further enhances the adsorption of MB dye which is beneficial for water treatment technologies. Hence, this study is looking forward to contribute for the knowledge in mesostructured silica researches.

1.6 Thesis Outline

This proposal reported the synthesis of mesostructured silica nanoparticles and its modification with CNT, which then studied towards methylene blue adsorption from aqueous solution. This proposal was divided into five chapters. Chapter 1 introduces the background of the research, problem statement and hypothesis, objectives of study, scopes of study, its significance, and lastly thesis outline for this study.

In chapter 2, the literature related to this study was reviewed. They consist of an overview of the mesostructured silica and carbon nanotubes material since they were discovered and their special features to be developed as potential adsorbents. Then, the vicinity of adsorption study was elaborated to obtain a deep understanding, such as equilibrium study, kinetics, and thermodynamics.

Chapter 3 explains the research design and methodology utilized in order to complete this work. This chapter describes the material used, experimental procedure, characterization methods, and adsorption study of adsorbents.

Chapter 4 discusses the experimental results performed in this study. First part explains the physicochemical properties of all synthesized adsorbents by XRD, N₂ physisorption, FTIR, TEM, and FESEM. Next, their performances towards adsorption of methylene blue were observed. In this section, the effect of pH, adsorbents dosage, initial concentration of methylene blue solution, and temperature was studied, in line with the equilibrium isotherm, kinetic and thermodynamic view of the adsorption.

Chapter 5 describes the summary derived from these study and listed the future work to be executed in order to expand this potential materials and further contribute to the knowledge.

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