THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Advanced and Sustainable Environmental Engineering)

DEGREE

Advanced and Sustainable Environmental Engineering — **FIELD**

Engineering — **FACULTY**

TITLE: Dye Adsorption Combined with Advanced Oxidation Process Using Water Treatment Sludge

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THESIS

DYE ADSORPTION COMBINED WITH ADVANCED OXIDATION PROCESS USING WATER TREATMENT SLUDGE

THANATCHA POTIYA

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Advanced and Sustainable Environmental Engineering)
Graduate School, Kasetsart University
2014

Thanatcha Potiya 2014: Dye Adsorption Combined with Advanced Oxidation Process Using Water Treatment Sludge. Master of Engineering (Advanced and Sustainable Environmental Engineering), Major Field: Advanced and Sustainable Environmental Engineering, Faculty of Engineering. Thesis Advisor: Assistant Professor Peerakarn Banjerdkij, D.Tech.Sc. 103 pages.

Water treatment sludge obtained from Bangkhen water treatment was used as an adsorbent for methylene blue (MB) removal in a batch experiment under different conditions of initial dye concentration (100-1,000 mg/L) and solution pH (2-11). Water treatment sludge was prepared with physical and chemical modification; nitric acid, carbonized, carbonized-nitric acid modified sludge (NS, CS and CNS). All of sludge-adsorbents were characterized with SEM-EDX, FTIR, Zeta potential and BET surface area analysis. The unmodified sludge (S) and NS were selected for further study due to highest MB removal percentage (100 mg/L) with 99.86 and 100, respectively. MB removal percentage by S and NS was decreased with increasing of initial concentration and decreasing of pH. Adsorption data fit well with Langmuir isotherm and pseudo-second-order kinetic model (R^2>0.999). The maximum capacity of S and NS was 82.64 and 90.91 mg/g, respectively. MB adsorption is a monolayer adsorption and chemisorption process which involves valence force. Intra-particle diffusion is involved in the adsorption process. There are three stages in adsorption process; macro pore diffusion, micro pore diffusion and surface film diffusion. Adsorption process by S and NS was also carried out with Fenton-like process to improve the efficiency in MB removal. Removal percentage of S and NS in adsorption process is 41.02 and 42.82, respectively. However, adsorption combined with Fenton-like process of S and NS is 48.89 and 99.96, respectively. Textile wastewater treatment was treated by S and NS adsorption with and without Fenton-like process. COD values after treatment of all experiments agree with industrial effluent standards (<120mg/L).

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Student's signature Thesis Advisor's signature

ACKNOWLEDGEMENTS

I would like to grateful thank to Asst. Prof. Dr.Peerakarn Banjerdkij my thesis advisor and Dr. Nuttaporn Pimpha in National Nanotechnology Center (NANOTEC) National Science and Technology Development Agency (NSTDA) my thesis co-advisor as well as the rest of my committee members for their advice, kindness, support and patience. Working under their supervision has been a rewarding learning experience, and I am very thankful to them for many fruitful discussions I received during my research as well as the knowledge they have imparted to me.

I would sincerely like to thank Assoc. Prof. Dr. Sanya Sirivithayapakorn my examination chairpersons and Assoc. Prof. Dr. Benjaphorn Prapagdee my external examiners for their devote time, valuable comment and suggestion. I would like to thank Prof. Nobuaki Otsuki for suggestion. I would like to thank Assoc. Prof. Dr.Thongchai Rohitatisha Srinophakun, the program director for many suggestion and comments and I would like to thank Ms. Sucheela Polruang, Lecturer of department Environmental Engineering for suggestion. I would like to truly thank Mr. Ruch Saiviwat and Mr. Banchong Ploychankul for their suggestion about textile wastewater.

I am grateful for the opportunity to be a priceless scholarship student of National Science and Technology Development Agency (NSTDA), Thailand, in Advanced and Sustainable Environmental Engineering of Thailand Advanced Institute of Science and Technology and Tokyo Institute of Technology (TAIST-Tokyo Tech) program.

I am especially appreciated my parents for their continuing encouragements.

Thanatcha Potiya

December 2014

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LIST OF ABBREVIATIONS

BET	=	Brunauer-Emmett-Teller
CNS	=	Carbonized and nitric acid modified sludge
COD	=	Chemical oxygen demand
CS	=	Carbonized modified water treatment sludge
FTIR	=	Fourier transforms infrared spectroscopy
MB	=	Methylene blue
NS	=	Nitric acid modified water treatment sludge
S	=	Unmodified water treatment sludge
SEM-EDX	=	Scanning electron microscope with energy dispersive X-ray
TOC	=	Total organic carbon

DYE ADSORPTION COMBINED WITH ADVANCED OXIDATION PROCESS USING WATER TREATMENT SLUDGE

INTRODUCTION

The extensive use of dyes in industry creates significant problems due to the discharge of colored wastewater. Various kinds of synthetic dyes appear in the effluents of wastewater in various industries such as dyestuff, textiles, leather and paper. Even if the presence of dye amount is very small, it is visible and affects the water quality (Nigama, 2000). Dyes contaminated discharge causes high biochemical oxygen demand (BOD) concentration which dictates to water pollution (Cheung *et al.*, 2009). Existed concerns are unsatisfied color and toxicity to aquatic creatures (Chiou and Li, 2003). Dyes can be divided based on chemical structure into several criteria such as anionic and cationic dyes or basic and acid dyes. This indicates that it is difficult to treat dye effluents because of their aromatic structures, which are non-biodegradable. Therefore the removal of color synthetic dye from effluents becomes important environmental issue (Sotelo *et al.*, 2002).

There are various dyes used in mentioned industries, and most of them are applied in coloring process. Cationic dyes which are commonly used are Methylene blue (MB) and Crystal violet (CV); whereas, anionic dye are Congo Red (CR) and Reactive red (RR). They cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea (Hameed *et al.*, 2007). Cationic dye such, CV is often used in gram staining while the others are generally used for dyeing cotton, silk, and wool. MB has been used as an adsorption testing model of dye from aqueous solution for a long time (Almeida *et al.*, 2009).

Among several chemical and physical methods, an adsorption process is one of the effective techniques that has been successfully applied for color removal from wastewater. Many adsorbents have been tested to minimize dye concentration in aqueous solution (Dogan *et al.*, 2007). Adsorption process provides high quality of

treated effluent if the wastewater treatment system for dye removal is efficiently and accurately designed (Martin *et al.*, 2003). Because of high adsorption capacity of activated carbon, it has been widely used in wastewater treatment. But it is costly and very limited in its application. Several low-cost adsorbents have also been tried for dye removal such as peat, activated slag, bottom ash, red mud, rice husks, carbon slurry and etc. (Crini, 2006).

Sludge has been widely applied as a material on many areas in last few decades. Sludge is by product from many manufactories processed entitled according to the process. For example, by product from water treatment process is called water treatment sludge. The amount of water treatment sludge is 70% of the generated waste from water treatment plant. Water treatment sludge composes of alum, iron and polymeric sludge depended on applied coagulant. Several thousand tons of water treatment sludge is discarded in a year in Thailand (Khorboot, 2003). Water treatment sludge has been applied for treatment of some waste such as textile wastewater, heavy metal and phosphate (Kayrranli, 2011). However, the efficiency of sludge in cationic dye treatment is still limited. To enhance the efficiency of sludge, advance oxidation process is applied in combination with adsorption process. Advance oxidation process called Fenton process is well-known for dye wastewater degradation. Moreover dye removal efficiency is enhanced when solid media is immobilized and activated with Fe solution to prepare Fe-supporting material. Fe-supporting material is used as a catalyst for dye degradation. This process is called as a heterogeneous Fenton-like process. Water treatment sludge is also used as solid media with Fenton's reagent in dye removal (Chu, 2001).

The aim of the study is to investigate the effect of initial Methylene blue (MB) concentrations and initial pH solution on the adsorption process of different group of before and after sludge modification. The equilibrium kinetic and isotherm data of the adsorption process are evaluated to study the methylene blue adsorption mechanism. Fenton like process is studied in combination with adsorption in this research to enhance the MB removal efficiency. Lastly, the authentic textile wastewater from textile industries is tested to determine feasibility of applying unmodified and modified water treatment sludge in the real treatment site.

OBJECTIVES

The objectives of this study are:

1. To study the adsorption mechanism of methylene blue in aqueous solution onto unmodified and modified water treatment sludge.

2. To study adsorption isotherm and kinetic of water treatment sludge between with and without modification.

3. To study Fenton-like process in combined with unmodified and modified water treatment sludge in MB aqueous solution adsorption.

4. To examine feasibility in applying unmodified and modified water treatment sludge combined with Fenton-like process for authentic wastewater from textile industry.

Scopes of work

Scopes of work in this study:

1. Wastewater in this study is synthetic wastewater and prepared by dissolving accurately weighed amount of MB in distilled water.

2. Sludge is used as adsorbent and it is collected from Bangkhen Water Treatment Plant.

3. The experiments were carried out using batch experiment in laboratory scale at National Nanotechnology Center, National Science and Technology Development Agency.

4. Water treatment sludge was modified with physical and chemical technique using carbonization and impregnation of nitric acid.

5. Adsorbent characterization was carried out using scanning electron microscope with energy dispersive X-ray using analysis (SEM-EDX), Brunauer-Emmett-Teller (BET) technique, zeta potential measurement.

6. Experimental conditions carried out for studying initial MB concentration and pH are in the range of 100-1,000 mg/L and 2-11, respectively. The fixed condition of adsorbent loading is 1 g, and volume of MB solution is 200 ml.

7. Textile wastewater experiment conducted in batch experiment was supported by K.World textiles industry.

8. Three indicators used to monitor color removal efficiency are percentage removal, TOC, and COD. These indicators were conducted by UV-vis spectrophotometer, high-temperature combustion method (TOC analyzer), and close reflux (Titrimetric method) respectively.

LITERATURE REVIEW

1. Adsorption

1.1 Adsorption process

Adsorption is integral to a broad spectrum of physical, biological, and chemical processes and operation in the environmental field. Adsorption also is a fundamental process in the physiochemical treatment of municipal wastewater, a treatment which can economically meet today's higher effluent standards and water reuse requirements. Adsorption is now viewed as a superior method for wastewater treatment and water reclamation (Weber, 1990). Application of adsorption for environmental management is well known. Application in wastewater treatment is demonstrated to be widely effective for removal of dissolved organic substances in wastewater (Droste, 1997).

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable substance comes into contact with a solid with a highly porous structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be deposited at the surface of solid. The solute retained (on the solid surface) in adsorption processes is called adsorbate, while the solid is called as an adsorbent. This creates forms the basis of separation by adsorption technology (Khorboot, 2009).

1.2 Type of adsorption

Adsorption process is generally classified in three groups:

Exchange adsorption: electrostatic due to charged sites on the surface. Adsorption goes up as ionic charge and as hydrated radius goes down.

Physical adsorption: weak Van der Waals attraction between adsorbate and adsorbent. The attraction is not fixed to a specific site and the adsorbate is

relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer adsorption.

Chemical adsorption: involves exchanging of electron between the surface of adsorbent and the molecule of adsorbate which resulting in a chemical reaction. The bond between both is much stronger than exchange adsorption and physical adsorption. Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible.

Table 1 Comparison of physical and chemical adsorption.

Parameter	Physical adsorption	Chemical adsorption
Force	Van der Waal's forces	Chemical bonding forces
Temperature	Usually occur at low temperature and decrease when temperature rising	Usually occur at high temperature
Reaction	Reversible reaction	Irreversible reaction
Phase in adsorption	Multilayer or monolayer	Monolayer only
Activation energy	Not require activation energy	Require activation energy
Specificity	Not specific	Highly specific
Heat of adsorption	Low heat usually 20-40 $kJmol^{-1}$	High heat usually 40-400 $kJmol^{-1}$

Source: Amrita Vishwa Vidyapeetham University (2013)

1.3 Adsorption mechanism

The adsorption mechanism involves about a solid phase (adsorbent) and a liquid phase (adsorbate) such as metal ions, organic substances. As the high affinity of the adsorbent and the adsorbate, the adsorbates are induced to the solid phase and bound through various adsorption mechanisms. Whereas adsorbate is gradually being

adsorbed, desorption of adsorbate occur simultaneously by the rate of adsorption and desorption are equal (Figure 1).

$$M^{n+} + LH \longrightarrow M^{n+}\text{-}L + H^{+} \qquad (1)$$

The reaction can be used to describe interaction between adsorbent and adsorbate. Adsorbate will be adsorbed on the binding sites which contained the function groups which have electron to form with adsorbate ion. Binding should express of result complex interaction which involves ion exchange, Van der Waals force, and coordinate complexes formation (Lawson *et al.*, 1984).

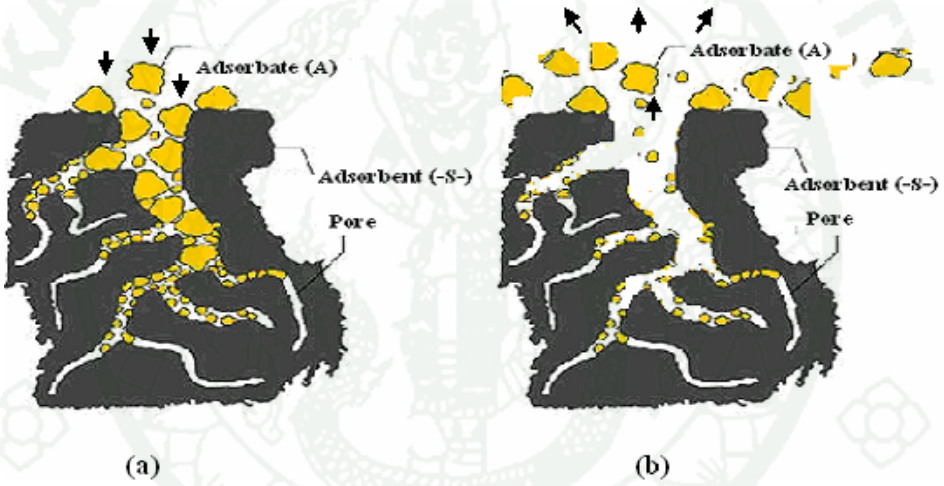


Figure 1 (a) Adsorption and (b) Desorption of adsorbate on the adsorbent

Source: Nokkaew (2008)

Adsorption mechanism has several steps which this is described in Figure 2 by Bansal and Goyal (2005):

1) Bulk Solution Transport: adsorbate transport from the bulk solution to the boundary layer by diffusion

2) Film Diffusion: adsorbate transport through thin film of liquid which around the adsorbent particle by molecular diffusion. Transport time and distance depend on liquid flow rate or turbulence in bulk solution.

3) Internal transport or Pore diffusion: after molecule transport to the thin film of adsorbent, the adsorbate molecule will transport into the pore of adsorbent. Interparticle transport may occur through pore diffusion or surface diffusion.

4) Adsorption: when the adsorbate molecule access to the adsorbent surface, the adsorption bonding between adsorbent and adsorbate will occur rapidly for physical adsorption. Hence, any steps serve as eliminator various molucules from solution. For chemical adsorption, it occurs changing naturally of adsorbed molecule.

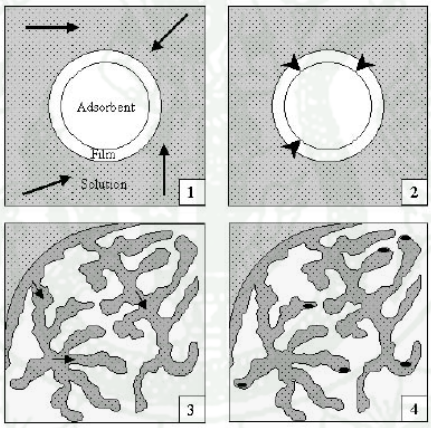


Figure 2 Adsorption mechanism

Source: Jungtiyanont (2003)

1.4 Adsorption factor

The most important factor affecting adsorption is divided into six factors (Junlaoun, 2007; Chairattanawatt, 2009; Kumar *et al.*, 2004).

Surface area: the surface area and porous structure of adsorbent is affecting in the adsorption efficiency. Larger sizes imply a greater adsorption

capacity. Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent.

Solubility: the solubility of adsorbate significantly influences the adsorption. The more hydrophilic a substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be adsorbed. It mean that the adsorption is reverse variation with the solubility of adsorbate.

pH: the pH of solution affect the extent of adsorption, because the distribution of surface charge on the adsorbent can be changed. Because of composition of adsorbent and activation technique, the adsorption efficiency base on functional group of the adsorbent. For example Patil (2011) showed that adsorption of methylene blue on teak tree (*Tectona grandis*) bark powder increased from 120 to 246.2 mg/g by variation in pH from 3 to 11. Because the methylene blue is a cationic dye so the adsorption decrease when pH lower than 5 resulting the adsorbent is a positive charge.

Temperature: When the solution temperature increase, the rate of adsorption will be increased while the adsorption capacity decrease because the reaction is exothermic reaction.

Contact time: The longer time for adsorption enhance removal efficiency. However, the equipment for adsorption operation will be larger.

Turbulence: The rate of adsorption depends on the molecular transport including film diffusion and pore diffusion. If low turbulence, film which surrond the adsorbent is more thickness and it is obstacle to transport of adsorbate molecule into the adsorbent. On the other hand, the high turbulence affects to decreasing of film thickness resulting the adsorbate molecule is easily transport to the adsorbent.

1.5 Adsorption kinetic

Experiment of adsorption kinetic, the solution sample was taken at regular time interval and concentration of sample was measured. The graph of adsorption was plotted between X/M and C_e shown in Figure 3. The adsorption capacity at any time and equilibrium time (mg/g) was calculated by following equation.

$$q_t = \frac{X}{M} = \frac{(C_o - C_t)V}{M} \quad (2)$$

where q_t is the amount of adsorbate adsorbed per unit mass of adsorbent at the any time (mg/g).

X is the amount of adsorbate (mg).

M is mass of adsorbent (g).

C_o and C_t are the liquid-phase concentration of adsorbate at initial and any time t, respectively (mg/L).

V is the volume of solutions (L).

$$q_e = \frac{X}{M} = \frac{(C_o - C_e)V}{M} \quad (3)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).

C_e is the liquid-phase concentration of adsorbate at the equilibrium (mg/L).

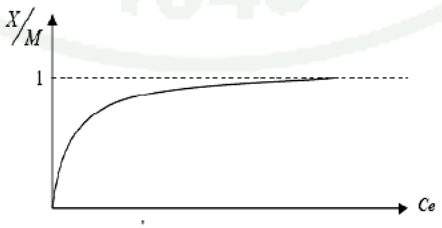


Figure 3 The graph of adsorption was plotted between X/M and C_e

Source: Watt (1997)

1.6 Adsorption isotherm

Adsorption isotherm shape is described by Masel (1996). It may be divided into six types which refer as the Bruanauer, Deming, Deming, and Teller (BDDT) classification (Figure 4).

Type I: it described monolayer adsorption. It usually is called Langmuir type. This adsorption isotherm is rarely discovered on nonporous materials. It represents the complete filling of micropores at a relative pressure less than unity ($P/P_0 << 1$) and it would be expected for reversible chemical adsorption. Example of Type I is the adsorption of nitrogen (N_2) or Hydrogen (H_2) on a charcoal at temperature near to -1800^oC.

Type II: it shows large deviation from Langmuir isotherm. It is S-shaped isotherm and discovered on nonporous material. This isotherm corresponds with monolayer adsorption. The intermediate flat region in the isotherm corresponds to monolayer formation. Example of Type II is the adsorption of nitrogen gas (N_2) at -1950 ^oC on Iron (Fe) catalyst and at -1950^oC on silica gel.

Type III: the forces of adsorption are relatively weak. It shows large deviation from Langmuir model. This isotherm explains the multilayer formation. There is no flattish portion in the curve so this indicates that monolayer formation is missing. Example of Type III is Bromine (Br_2) at 790^oC on silica gel or Iodine (I_2) at 790^oC on silica gel.

Type IV: This adsorption isotherm is rarely discovered on porous materials. It is similar to type II at low values of P/P_o. At high values of P/Po, the adsorption increase which pore or capillary condensation occur. It may be used to determine a pore size distribution. This type corresponds to monolayer formation. Example of Type IV is adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500$_o$C.

Type V: It is similar to type III, but capillary condensation occurs at high value of P/P_o. Example of Type V is adsorption of water on a charcoal at 1000^oC.

Type VI: It is seldom found. The shape of isotherm depends on the system and temperature.

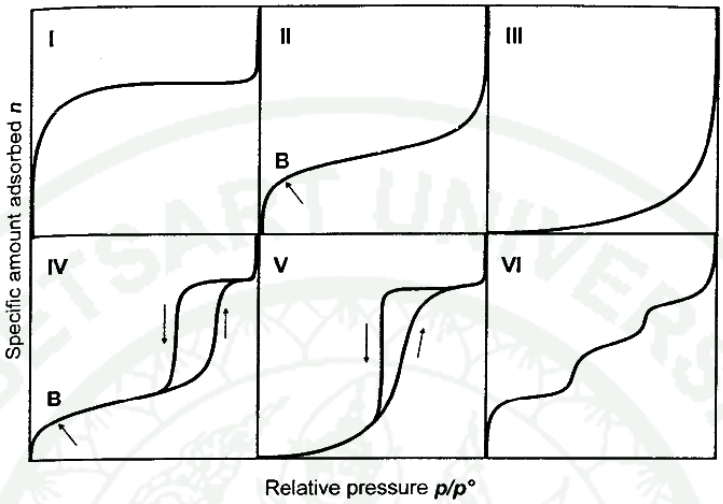


Figure 4 The six shape type of adsorption isotherm

Source: Masel (1996)

Adsorption process is usually studied through graphs known as adsorption isotherm. Adsorption isotherm is the illustration of the amount of adsorbate adsorbed per unit weight on adsorbent as a function of the equilibrium concentration in the solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.

1.6.1 Langmuir adsorption isotherm

Langmuir adsorption model is used to quantify the amount of adsorbate adsorbed on the adsorbent as a functional of concentration or partial pressure at a given temperature. It based on four assumptions.

-The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.

- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The linear of Langmuir isotherm equation is expressed as:

$$q_e = \frac{Q_o b C_e}{1+bC_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (5)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L).

q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium time (mg/g).

Q_o is the maximum loading of adsorbate on adsorbent (mg/g).

b is the energy constant of Langmuir adsorption isotherm (L/mg).

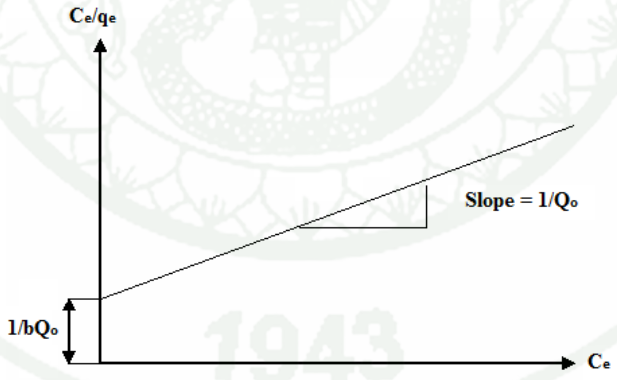


Figure 5 The Langmuir adsorption isotherm plot between C_e/q_e and C_e

Source: Nokkaew (2008)

The Langmuir adsorption isotherm plot between C_e/q_e and C_e is shown in Figure 5. Moreover, this plot also gives straight line with slope $1/Q_o$ and with intercept $1/bQ_o$.

1.6.2 Freundlich adsorption isotherm

Freundlich adsorption isotherm is an empirical equation and no physical basis. This isotherm assumes heterogeneous surface energies. It will give result exactly when the adsorption is clearly physical process without any change in the adsorbed state. Freundlich equation is expressed by following equation.

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (7)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium time (mg/g).

C_e is the equilibrium concentration of the adsorbate (mg/L).

K_F is the constant of Freundlich isotherm which related to adsorption capacity.

n is the constant of Freundlich isotherm which related to adsorption intensity.

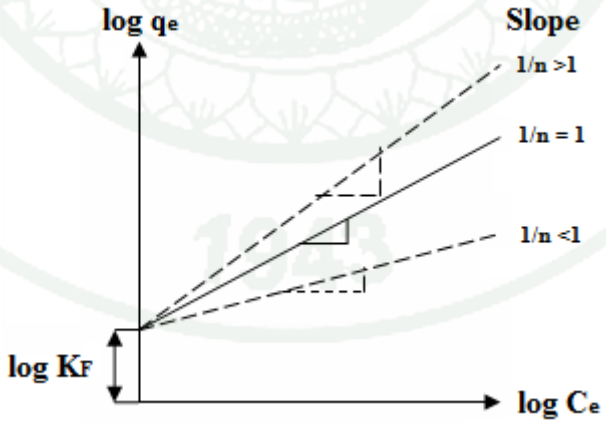


Figure 6 The Freundlich adsorption isotherm plot between log q_e and log C_e

Source: Nokkaew (2008)

1.7 Adsorption kinetic model

A better understanding about adsorption mechanism and rate which the contaminant was removed from aqueous solution is crucial to design adsorption treatment process. In order to investigate mechanism and adsorption rate, the pseudo-first-order, pseudo-second-order and intra-particle models were used to fit the adsorption data. These models describe the dye adsorption as well as other contaminants (heavy metal) on adsorbent. Parameter in these models was estimated from the experiment adsorption data with the promoting of the non-linear curve fitting method.

1.7.1 Pseudo-first-order model

The simple kinetic model of adsorption is the pseudo-first-order rate which expressed by following equation. This model is more suitable for low concentration of adsorbate.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium time (mg/g).

q_t is the amount of adsorbate adsorbed per unit mass of adsorbent at the any time (mg/g).

k_1 is the rate constant of pseudo-first-order model (h^{-1}).

t is time (h)

The plot between log (q_e-q_t) and t should give a straight line with slope -k_1/2.303 and intercept log q_e. The experimental q_e values did not agree with the

calculated q_e values, gained from the linear plot, indicating that the adsorption does not fit with pseudo-first-order model.

1.7.2 Pseudo-second-order model

Adsorption reaction fit with the pseudo-second-order model is dependent on the amount of adsorbate adsorbed on the adsorbent surface and the amount of adsorbed at equilibrium. The pseudo-second-order model is expressed by following equation.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 is the rate constant of pseudo-second-order model (g/mg.h).

The pseudo-second-order constant (k_2) and the equilibrium adsorption capacity (q_e) can be obtained from the plot between t/q_t and t that should show in linear plotting.

1.7.3 Intra-particle diffusion model

The adsorption mechanism can be explained by the intra-particle diffusion model. Weber and Morris (1963) defined that if the rate controlling factor is intra-particle diffusion, the uptake of adsorbate varies with the square root of time. This model is shown in equation 12.

$$q_t = k_i t^{1/2} + C \quad (12)$$

where k_i is the intra-particle diffusion constant (mg/g.min).

According to equation 12, the plot between q_t and $t^{1/2}$ should give straight line with a slope k_i and intercept C when adsorption mechanism is followed with the intra-particle diffusion model. Value of intercept gives an idea of the thickness of boundary layer. If this plot passes through the origin (C=0), this means the only intra-particle diffusion is controlling step. However, the plot does not pass through the origin, it indicates that the adsorption process is rather complex and other processes would control the adsorption rate (Alzaydien, 2009).

Rodriquez *et al*. (2009) used the activated carbon as adsorbent for removal of anionic and cationic dye. The result fit well with Langmuir isotherm and pseudo second order kinetic model. Almeida *et al.* (2009) studied adsorption of methylene blue on montmorillonite clay under batch experiment in different parameter and the result revealed that the experiment data fitted well with Langmuir isotherm and pseudo-second-order model. Indian rosewood sawdust was used as adsorbent for methylene blue adsorption in batch experiment. Initial reaction was fast within 30 minutes and at the neutral pH showed that higher adsorption. It was also studied commercial activated carbon to compare efficiency with Indian rosewood (Garg *et al*., 2004). Patil *et al.* (2011) studied adsorption of methylene blue using teak tree (*Tectona grandis*) as adsorbent. The adsorption capacity of teak tree powder (TTB) was 333.33 mg/g and the adsorption isotherm fit with both Langmuir and Freundlich isotherm including pseudo-second-order model. The adsorption is a physical adsorption and a spontaneous process.

2. Adsorbent

Adsorbent for adsorption technique is used widely to remove pollutant from wastewater. Among all adsorbent material, activated carbon is the most popular for pollutant removal in wastewater (Babel and Kurniawan, 2003). Although activated carbon has the several advantages, it is quite expensive for maintenance, regeneration of saturated carbon. Therefore research in recently year is interest in the production of alternative adsorbent which low cost and easy to maintenance. Attention has focused on the natural solid support which ability to remove pollutant at low cost operation. Cost is actually an important parameter for operation (Aydin, 2008).

Adsorbent type is classified into natural adsorbent and synthetic adsorbent. Natural adsorbents include charcoal, clays, clay minerals, and zeolites (Bousher, 1997). These natural materials are relatively cheap, abundant in supply and have significant potential for modification of their adsorption capability. Synthetic adsorbents are prepared from agricultural products and wastes, industrial wastes, domestic wastes, sewage sludge and polymeric adsorbents (Crini, 2006). Each adsorbent has different characteristics such as pore structure, porosity and nature in adosorption. Many waste materials include fruit wastes, coconut shell, egg shell, scrap tyres, bark, sawdust, water hyacinth, rice husk, banana pith, fertilizer wastes, activated palm ash, fly ash, furnace slag, chitosan and seafood processing wastes, seaweed, peat, bamboo, clays, red mud, bio-sludge, zeolites, sediment and soil, montmorillonite etc (Rafatullah *et al.*, 2010; Junlaoun, 2007; Baybars, 2012; Namasivayan *et al.*, 1993).

2.1 Pore structure and surface of adsorbent

International Union of Pure and Applied Chemistry (IUPAC) classify pore structure base on its width which represents the distance between the walls of a slit-shaped pore or the radius of a cylindrical pore. Pore type classification is grouped into three types as micropores, mesopores, and macropores (IUPAC, 1995). It is shown in Figure 7.

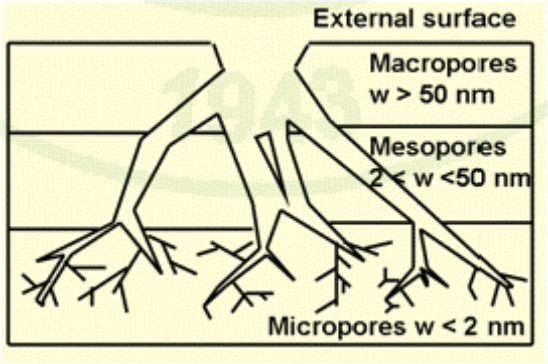


Figure 7 Pore type classification

Source: Khorboot (2009)

Micropores are considered to have a pore size less than 2 nm and to exhibit apparent surface areas usually higher than 200 to 300 $m^2g^{-1}$and pore volume is approximately between 0.15 to 0.70 cm^3/g. Adsorption in micropores occurs through volume filling and it has no capillary condensation appearance. The adsorption energy of micropores is higher when compare with larger pores.

Mesopores are considered to have a pore size less than 50 nm but more than 2 nm width. Pore volume is approximately between 0.1 and 0.2 cm^3/g.

Macropores are not important for adsorption because of very small surface area (0.5 m^2/g). They have a pore size more than 50 nm and a pore volume between 0.2 and 0.4 cm^3/g.

2.2 Adsorbent characterization

To remove pollutant from wastewater, the adsorbent should fulfill following these criteria (Jungtiyanont, 2003).

1) The uptake and release of pollutant should be efficient and rapid

2) Adsorbent should be low cost and easily to reuse.

3) Adsorbent removal from solution should be rapid, inexpensive, and efficient because long time removal will increase cost of operation.

4) Adsorbent should have availability to adsorb several pollutants because the discharged wastewater contain a lot of pollutant.

5) Separation of pollutant from the adsorbent should be selective, economically feasible and minimal adsorbent loss.

6) The regeneration of adsorbent should be easily operation using the effective reagent and the regenerated adsorbent can be used repeatedly.

3. Dye

Dye is a colored substance which widely applied in many industries such as textile, leather, paper, plastic, food, cosmetic, mineral processing. Dyes have a different color when they are dissolved, because they adsorb light at different wavelength.

3.1 Classification of dye

Dye is not only made from natural material but it also can be synthesized as a synthetic dye. Dye can be classified according to chemical structure and application method. It is difficult to classify each dye type because of overlapping of both chemical type and application method. Major classification of dye is acid, basic and direct dye (Knutson, 2004).

Acid dye (Anionic dye): Acid dye was the synthetic dye for wool. It is called acid dye because bath for dyeing have to be acidic. It is a suitable condition for attaching fiber. When it is dissolved, charge are displayed a negative charge. Acid dye is not used in cellulose coloring.

Basic dye (Cationic dye): Basic dyes are preferred for directory and newsprint paper with high lignin content Basic dye are soluble. Difference of basic and acid dye, basic dye contains the cationic portion. It is often applied in paper coloring process hence it is low cost substance.

Direct dye: Direct dyes are used to color paper with the low lignin content. Direct dye is directness and simplicity application with cotton, flax, and rayon. It is moderate in cost and easy to apply. Limitation of direct dye is coloring textiles.

3.2 Disadvantage of dye

Dyes are classified be organic pollutant. Therefore discharging of coloring wastewater to the environment is seriously problems. Some dyes are made from

carcinogenic substance such as aromatic compound and benzidine. They are difficult to be biodegraded because of synthetic origin and aromatic structure. Therefore, primary and secondary wastewater treatment are not suitable to treat these effluent. Some dyes are toxic to aquatic life, microbial population. Dyes can reduce penetration of light into the water body resulting reducing of photosynthesis in aquatic plant which usually produce oxygen for aquatic life. They also cause damage to health such as dysfunction of brain, nervous system, liver, reproductive system, and kidney (Che Ani, 2004; Rashed, 2013; Dogan *et al*., 2007; Maghri *et al*., 2012).

Table 2 Classification of Dye

Classification type	**Dye**
Solubility	Soluble dyes (anionic or cationic)
	Disperse dyes (non-ionic, slightly soluble)
	Pigment (insoluble)
Application method	Acid dye (anionic)
	Basic dye (cationic)
	Direct dye
	Azoic dye
	Sulfur dye
	Reactive dye
	Disperse dye
Chemical composition	Azo dye and pigment (mono azo, diazo, etc.)
	Anthraquinone dye
	Benzodifuranone dye
	Polycyclic aromatic carbonyl dye
	Nitro and Nitroso dye
	Styryl dye
	Phthalocyanines
	Quinophthalones
	Miscellaneous dye (Stilbene and Formazan dye)

Source: Knutson (2004)

3.3 Dye wastewater Treatment

Many industries create a huge amount of wastewater which has component with high organic concentration and high color concentration. This indicates that wastewater is high biological oxygen demand (BOD). Several technologies treatment for wastewater are applied and developed to find an efficient and economic way to treat appropriately the dye wastewater which contain high BOD, including physical, biological, chemical treatment, and other treatments. These technologies are usually highly efficient for the dye wastewater.

Many physical, chemical, biological treatment for color removal have been applied including flotation, coagulation and flocculation, Fention reaction, ozone oxidation, adsorption, membrane separation (reverse osmosis), activated sludge process, etc. These treatments are shown in Table 3.

3.4 Methylene blue

3.4.1 Characterization

Methylene blue (MB) is a heterocyclic aromatic compound. The formula is $C_{16}H_{18}ClN_3S$. At room temperature, it appears as a solid, odorless that blue solution when dissolving in water. Characterization is shown in Table 4.

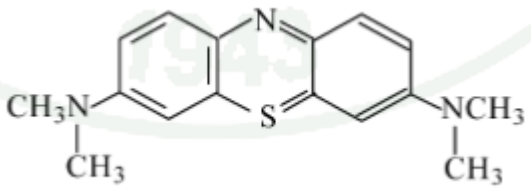


Figure 8 The structure of methylene blue

Source: Almeida (2009)

Table 3 Treatment technologies for dye removal

Treatment technology	Advantage	Disadvantage
Physiochemical treatment		
Coagulation and flocculation	Low cost and detention time, High efficiency	Require additional treatment such as separation process
Fenton process	High effective both soluble and insoluble dye	Problem with sludge disposal and high cost
Ozonation	Effective for azo dye removal	Release aromatic dye, short half like of ozone
Adsorption	Economically attractive treatment, effective	Require addition treatment such as separation process and regeneration
Ion exchange	Regeneration with low loss of adsorbent	Not effective for all dye type
Biological treatment		
Aerobic treatment	Partial or complete removal for all dye type	Expensive treatment, require aerator
Anaerobic treatment	Biogas from treatment is used as stream generation	Longer acclimatization
Advanced treatment		
Membrane filtration	Remove all dye type, recovery and reuse of dye	High cost, concentrated sludge production
Photocatalysis	Operation at ambient condition, short time treatment	Effective for small amount of dye. High cost

Source: Carmen (2012)

Table 4 Characterization of methylene blue

Characterization	
Formula	$C_{16}H_{18}ClN_3S$
Classification	Basic dye (cationic dye)
Molecular weight (g/mol)	319.85
Appearance	Solid
Melting point (°C)	100-110
pH	Acidic
Solubility	Soluble
Specific gravity	1.1

Source: Khorboot (2009)

3.4.2 Application and Toxicity

Methylene blue is widely used as a redox indicator in analytical chemistry, a photosensitizer to create singlet oxygen, a diagnostic agent, dye, indicator for cell measurement, a non-selective inhibitor, a medical use for malaria, staining, chemical treatment for aquaculture. Methylene blue cause adverse effect each pathway. It is shown in Table 5.

Table 5 Toxicity of methylene blue

Target organ	Toxicity
Eye	Eye irritation, chemical conjunctivitis
Skin	Skin irritation
Ingestion	Gastrointestinal irritation with nausea and vomiting
Inhalation	Respiratory tract irritation, cyanosis, methemoglobinemia

Source: Sigma Aldrich (2013)

4. Water treatment process

Currently, Metropolitan Waterworks Authority (MWA) has four water treatment plant including Samsen, Bangkhen, Thonburi, Mahasawat water treatment plant. Bangkhen water treatment plant is the highest production capacity at 3.2 x 10^6 m^3/day. Raw water used in MWA water treatment process is taken from Chao Phraya River. Turbidity of raw water is in range 15-160 NTU (Metropolitan Waterworks Authority, 2010).

In water treatment process need to coagulant for sedimentation of suspended solid. Alum and Ferric coagulant is used currently in water treatment plant because of their positive ions and inexpensive coagulant. When raw water is added alum, alum will react with water molecule.

$$Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+ \quad (13)$$

$$Al^{3+} + 2\,H_2O \longrightarrow Al(OH)_2^{+} + 2H^+ \quad (14)$$

$$7Al^{3+} + 17\,H_2O \longrightarrow Al(OH)_{17}^{4+} + 17H^+ \quad (15)$$

$$Al^{3+} + 3\,H_2O \longrightarrow Al(OH)_{3(s)} + 3H^+ \quad (16)$$

4.1 Treatment process

Raw water was treated to remove suspended solid by sedimentation and filtration, pathogen by adding chlorine solution. Treated raw water will be distributed to the domestic level. Bangkhen water treatment process is shown in Figure 9.

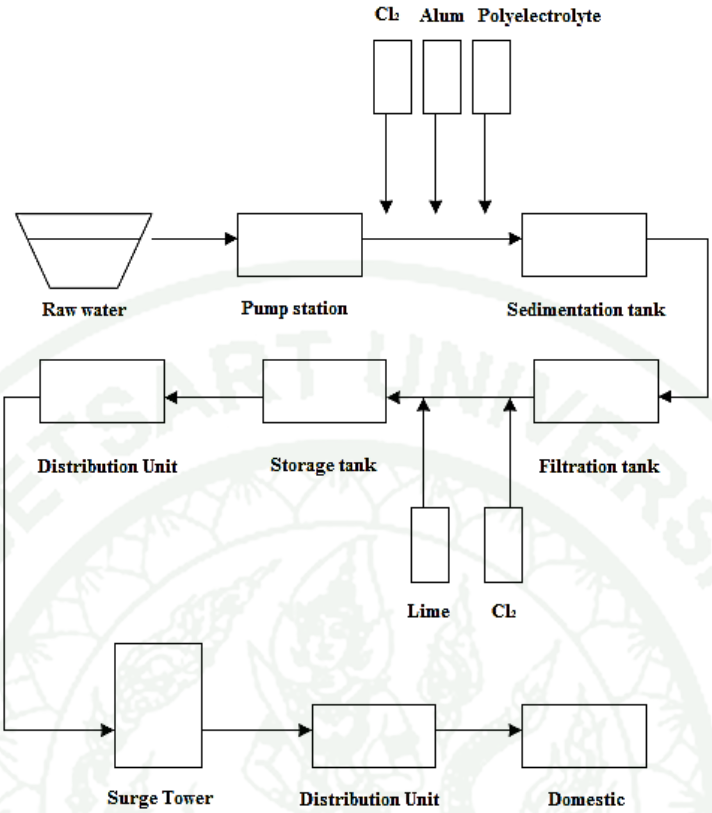


Figure 9 Water treatment process

Source: Kanjanamai (2003)

4.2 Sludge removal

Water treatment sludge is byproduct of water treatment process which alum or ferric coagulant are used to remove turbidity, color, and suspended solid. Alum and ferric coagulant is aluminum and iron based salt form, this indicates that the composition of the sludge is mostly aluminum and iron. Procedure of sludge removal from water treatment process is shown in Figure 10.

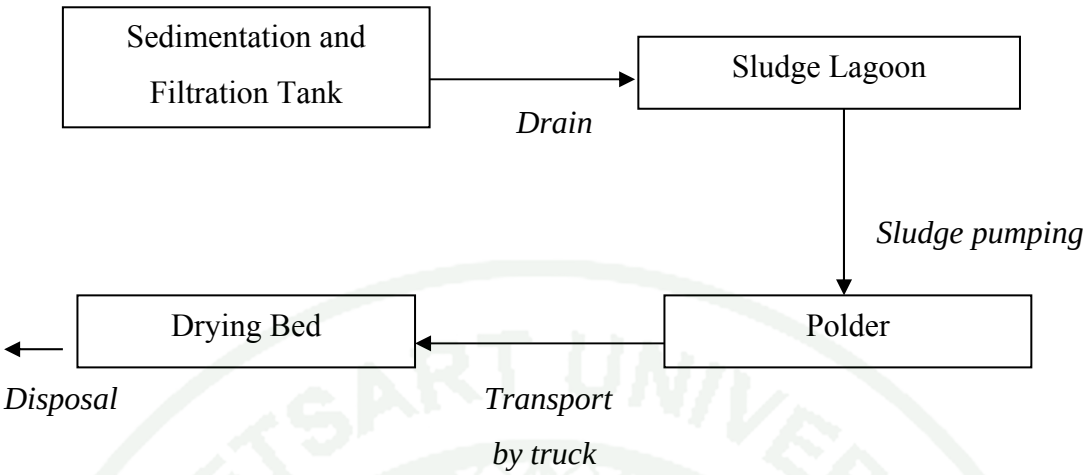


Figure 10 Sludge removal process

Source: Kanjanamai (2003)

Currently, several studies have focus on the utilization of sludge rather than dispose sludge. Makris *et al*. (2004) reported that water treatment sludge is high surface area and pore volume so it always used as adsorbent. Some researcher also investigate that sludge is appropriate to be used in a construction industry.

Kanjanamai (2003) reported that the study focus on the use of sludge as the main raw material in producing of baked brick. Chu (2001) investigated about dye removal from textile using Al-based sludge. Razali *et al*. (2007) use sludge as adsorbent in removal different phosphorus from aqueous solution. Putra *et al*. (2011) studied about soil remediation using sludge as an entrapping zone and the results showed that lead ion in contaminated soil will be entrapped in sludge. Makris *et al.* (2006) used aluminum-based drinking water treatment residuals as adsorbent for perchlorate removal.

5. Fenton process

Fenton process is one type of advanced oxidation process. Oxidation process is represented a widely used chemical method for textile wastewater treatment. Fenton process is mainly used as a pre-treatment stage. Fenton reaction is exothermic

reaction and usually used for organic pollutant degradation. The reaction is a redox reaction which Fenton reagent is added into the reaction. Fenton reagent refers to mixing of hydrogen peroxide (H_2O_2) and iron catalyst. Ferrous ion and hydrogen peroxide are oxidized to ferric ion (Fe^{3+}) and reduced to hydroxyl radical ($HO^{\bullet}$) respectively in Equation 17. Ferric ion can be reduced back to ferrous ion by hydrogen peroxide (Xue, 2009). This reaction is slower than initial reaction (Equation 18).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (17)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (18)$$

For the organic degradation, the optimal condition of pH is in range pH 3-4. Fenton reaction can be reached to high efficiency by UV irradiation, it is known as photo-Fenton reaction (Punzi, 2012). Fenton process can be operated both homogeneous and heterogeneous process. The homogeneous or Fenton process is involved only degradation process of organic pollutant and this reaction refers to Fenton reagent that it consists of hydrogen peroxide and only iron solution. Disadvantages of this reaction are the formation of recalcitrant intermediate which have ability to inhibit degradation and the production of iron sludge and it should be disposed which means an additional removal process (Wang, 2011). This can be solved by developing heterogeneous process. It is called as Fenton-like process due to co-operation of iron oxide into supporting material and hydrogen peroxide. Fenton-like process can be simply described that iron oxide, are adsorbed onto supporting material, and redox reaction between ferric and ferrous ion take place in the presence of hydrogen peroxide which encourage the formation of hydroxyl and perhydroxyl radicals (Ersoz, 2014). This case is easily shown by following equations, where *M* represents supporting material.

$$M\text{-}Fe^{3+} + H_2O_2 \longrightarrow M\text{-}Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (19)$$

$$M\text{-}Fe^{2+} + H_2O_2 \longrightarrow M\text{-}Fe^{3+} + OH^{-} + HO^{\bullet} \quad (20)$$

Several studies have investigated different supporting material catalyst for Fenton-like process such as zeolite, rice husk ash, goethite, clay or alum sludge (Tony *et al.*, 2009; Ramirez *et al*., 2010; Rache *et al*., 2014; Ersoz, 2014). Liu *et al*. (2007) investigate decolorization of direct dye, acid dye, and vat dye using Fenton and photo Fenton process. The result showed that Fenton process is high efficiency for three type dye. The efficiency of a photo Fenton process is slight higher than Fenton process for all dye.

Chungsiriporn *et al*. (2009) studied removal of wastewater from packaging industry using Fenton process. The initial of chemical oxygen demand (COD) and adsorbance of wastewater were 125-172 mg/l and 0.07-0.9 respectively. The result showed that COD and color removal efficiency were 35-40% and 90-95%, respectively. At dark atmosphere, the removal efficiency was lower than light atmosphere.

Soon and Hameed studied about an efficiency of the homogeneous and heterogeneous Fenton process, they explained that the heterogeneous or Fenton-like process was more effective for synthetic dye wastewater treatment due to using a lesser amount of hydrogen peroxide, highly catalytic activity and promoting kinetic reaction rate compared with the homogeneous process (Soon and Hameed, 2011).

Dutta *et al.* (2001) studied methylene blue removal using Fenton-like process. They carried out experiment under the effect of different parameter including initial dye concentration, ignition Fenton reagent dose (Fe^{2+} and H_2O_2), and temperature. The methylene blue can be degraded effectively in solution at 98% which in pH range 2.2-2.6 at 299 K.

MATERIALS AND METHODS

Materials

1. Raw material

Water treatment sludge was obtained from Bangkhen water treatment plant in sludge removal process

2. Chemicals

2.1_Methylene blue (Sigma-Aldrich)

2.2_Nitric acid, 65% (CARLO ERBA)

2.3_Hydrogen peroxide, 30% (CARLO ERBA)

2.4_Hydrochloric acid, 37% (CARLO ERBA)

2.5_Sodium hydroxide (CARLO ERBA)

2.6_Potassium dichromate (Fluka)

2.7_Silver sulfate (Sigma-Aldrich)

2.8_Iron (II) sulphate heptahydrate (Sigma-Aldrich)

2.9_1,10-phenanthroline monohydrate (Fluka)

3. Equipment

3.1_UV-vis Spectrophotometer (PerkinElmer, Lambda 650)

3.2_pH meter (Mettler Toledo, DG 115-SC)

3.3_Mechanical stirrer (IKA, RW 20 digital)

3.4_Analytical balance 4 digits (Mettler Toledo, XS 204)

3.5_Micropipette (eppendorf)

3.6_Zetasizer (Malvern, Nano ZSP)

3.7_Vaccum pump (Vaccumbrand, CVC 2)

3.8_Hot Air Oven (Memmert, UNE 200)

3.9_Surface area and pore size analyzer (BEL Japan, BELSORP)

3.10 Furnace (Nabertherm, LT15113)

3.11 Sieve mesh 50 μm

3.12 Syringe filter PTFE (13 mm, 0.45 μm)

3.13 Scientific glassware

Methods

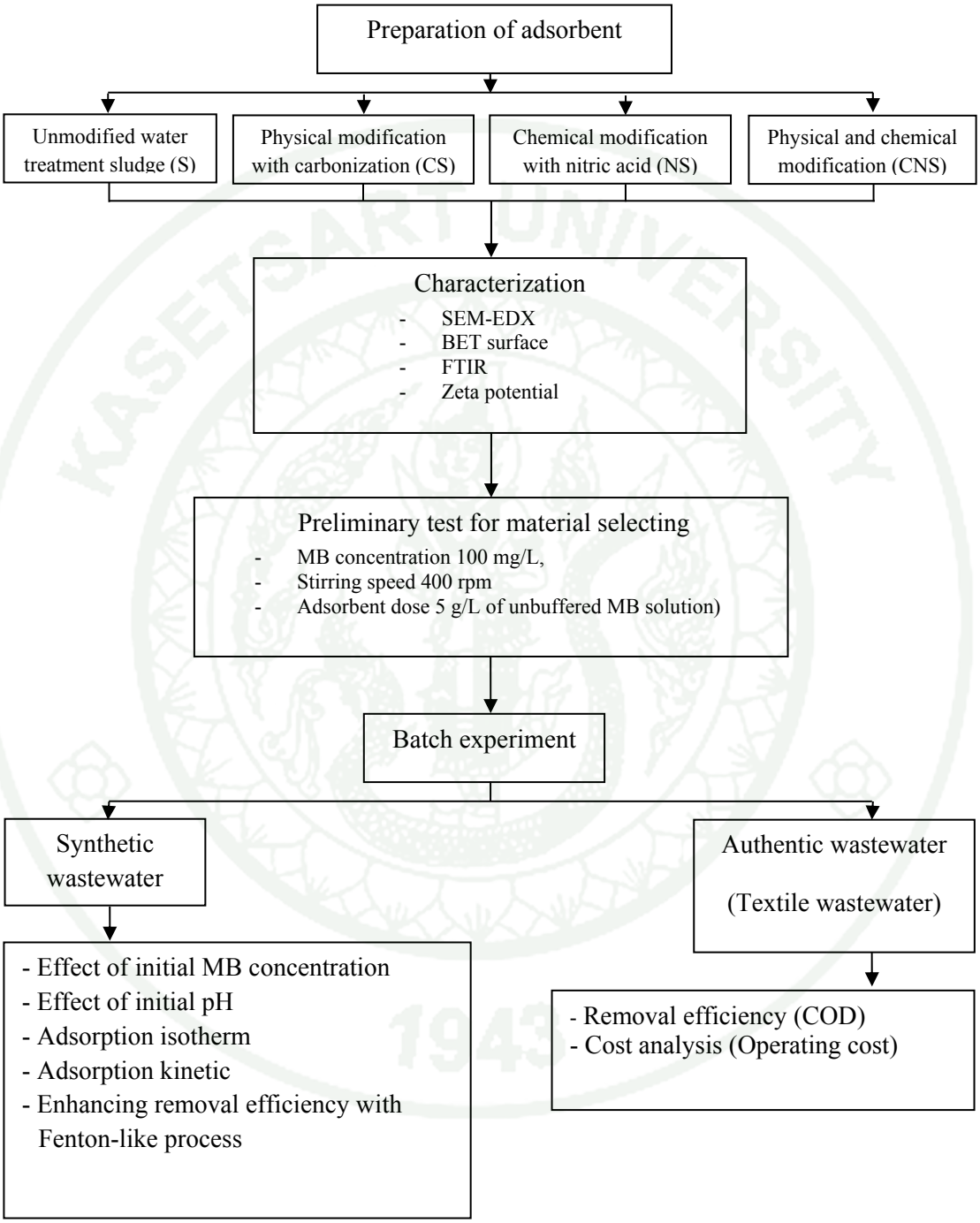


Figure 11 Schematic diagrams of the overall experiments

1. Experimental preparation

1.1 Preparation of synthetic wastewater

The wastewater was a synthetic wastewater which consisted of methylene blue ($C_{16}H_{18}CIN_3S$). Methylene blue was purchased from Sigma-Aldrich, it was used without further purification. Methylene blue solution was dissolved with distilled water and collected in volumetric flask which dried with hot oven.

1.2 Preparation of sludge-adsorbents

Water treatment sludge was obtained from Bangkhen water treatment plant. It was dried at 105ºC for 24 h and then sieved through a 50 μm sieve using ASTM standard sieve before to its use in the any experiment. After it was sieved, it was modified with different method including physical, chemical and physiochemical modification. For chemical modification, sludge was impregnated for 4 h with 800 ml of 1 M HNO_3, filtered and dried for 24 h, respectively. This method followed Zhang *et al*. (2012). Carbonization which is a popular physical process was used for modification. Sludge was carbonized in furnace with a constant heating rate of 15ºC/min and a holding time of maximum temperature 30 min at 700ºC (Smith *et al.*, 2009). All of sludge-adsorbents were characterized with SEM-EDX, FTIR, Zeta potential and BET surface area analysis.

2. Characterization

The samples were dispersed onto carbon tape prior to chemical characterization. Chemical component and morphology of S, NS, CS, and CNS were analyzed by scanning electron microscope/energy dispersive X-ray using analysis (SEM-EDX).

Surface area, total pore volume, and average pore diameter were analyzed with Brunauer-Emmett-Teller (BET) technique using BEL Japan, BELSORP series.

Prior to adsorption by N_2 gas as the adsorbate, the sample were out-gassed under vacuum at 60^{o}C.

Zeta potential measurement was carried out using Malvern zatasizer by salt addition method. At 50 ml of 0.1 M NaCl solutions was taken in the different flask. The pH of the solution was adjusted to 2, 4, 6, 8, 10, and 12 by adding small amount of 0.1M HCl and NaOH solutions. The result was plotted between pH of solution and zeta potential (Yang *et al.*, 2010; Mustafa *et al.*, 2002).

3. Synthetic wastewater experiments

The experiments were set in laboratory scale and batch experiment at room temperature. The previous studied (Jungtiyanont, 2003) had suggested that the temperature between 10^{0}C and 35^{0}C did not affect adsorption capacity. This study was divided into 3 parts. Firstly, all of adsorbent was studied about efficiency in MB removal to select the most suitable adsorbent for next experiment. Secondly, the suitable adsorbent was further investigated in term of initial MB concentration and pH compared with unmodified sludge. An adsorption isotherm, kinetic equilibrium and intra-particle diffusion were carried out to study mechanism. Finally, Fenton-like process was conducted in MB removal to compare removal efficiency with adsorption process.

3.1 Preliminary test for material selecting

To determine the efficiency of S, CS, NS, and CNS on the adsorption of methylene blue, 1 g of each sludge-adsorbent was added in 200 ml of MB solution (100 mg/l) into the double jacketed reactor. Adsorption was stirred with 400 rpm for 120 min at room temperature. The removal efficiency was indicator to select which adsorbent should be used for further procedure.

Figure 12 Double jacketed reactor with the mechanical stirrer

3.2 Adsorption study

After selection of sludge-adsorbents, the selected sludge-adsorbents were conducted under the different parameter.

3.2.1 Effect of initial MB concentration

The initial concentration of MB solution was varied at 100, 300, 500, 700, and 1,000 mg/l of MB solution. The experimental was conducted by addition 1 g of selected adsorbent into each 200 ml of the desired MB concentration. The experiment was carried out at room temperature and a constant speed of 400 rpm with the mechanical stirrer. Collecting of sample was withdrawn 4 ml from solution then filtrated with 0.45 μm syringe filter and diluted. The supernatant was measured using UV-vis spectrophotometer at maximum wavelength of 664 nm.

3.2.2 Effect of initial pH solution

The pH of solution containing 1,000 mg/L of MB was varied at 2, 7 and 11 by adding 0.1 M HCl and NaOH solution. The experimental was carried out as described in above section.

3.3 Adsorption with and without Fenton-like process

The amount of selected sludge was fixed at 1 g and added into 200 ml of MB solution (1,000 mg/l). The stirring speed and contact time was controlled at 400 rpm and 4 h. The reaction was set at room temperature. After adsorption 30 min, Fenton reaction took place when the addition 2 ml of H_2O_2 into the MB solution. The remaining amount of MB in the solution was analyzed with UV-vis spectrophotometer at 664 nm and TOC analyzer.

4. Authentic wastewater experiments

The authentic wastewater collected from K.World textile industry was investigated by adsorption combined with and without Fenton-like process. The experiment was conducted in batch system at room temperature. Batch experiments were carried out as described section 3.3. Removal efficiency was analyzed with COD closed reflux standard method.

5. Analytical methods

5.1 Removal percentage

The efficiency of MB removal was investigated by measuring the absorbance at 664 nm of UV-vis spectrophotometer. It was calculated following Almeida (2009).

$$\text{Removal percentage} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (21)$$

where C_o is liquid-phase concentration of adsorbate at initial time (mg/L).

C_t is liquid-phase concentration of adsorbate at any time t (mg/L).

5.2 The amount of adsorbate adsorbed on the adsorbent

The amount of adsorbate adsorbed on the adsorbent at any time and equilibrium time (q_e and q_t) was shown in Equation 2 and 3 respectively.

5.3 Adsorption isotherm, kinetic and intra-particle diffusion

Adsorption isotherm was investigated in this study. Langmuir and Freundlich model were fitted with adsorption data. These models are shown in Equation 5 and 7, respectively. The pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used in order to describe about adsorption mechanism. They are shown in Equation 9, 11 and 12 respectively.

5.4 Material cost evaluation

Material cost evaluation was calculated from electricity bill, tab water supply and chemical cost which based on Metropolitan Electricity Authority (MEA), Provincial Waterworks Authority (PWA) and chemical store, respectively. These costs are calculated to compare each sludge-adsorbent for suitable material selecting in wastewater treatment.

6. Place

National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathumthani, Thailand.

RESULTS AND DISCUSSION

1. Characterization of sludge-adsorbents

Water treatment sludge obtained from Bangkhen water treatment plant was used as an adsorbent for this study. It was prepared with different modification method. Table 6 shows the type of unmodified and modified sludge. All of sludge-adsorbents were characterized with SEM-EDX, FTIR and BET surface area analysis. The characteristic results were discussed as follows.

Table 6 Sludge-adsorbents type in this study

Type of sludge-adsorbents	Code	Apperance
Unmodified sludge	S	
Nitric acid modified sludge	NS	
Carbonized modified sludge	CS	
Carbonized and nitric acid modified sludge	CNS	

1.1 Morphology of sludge-adsorbents by Scanning Electron Microscope with Energy Dispersive X-ray (SEM/EDX)

The morphology of adsorbents was measured using scanning electron microscope (SEM). SEM images of all adsorbents were presented in Figure 13. The morphology images illustrate a variable size and irregular shape which the SEM results were not different. It can be observed that the adsorbents are dense and sheet without pore and surface development. This can be hypothesized that the dye adsorption on adsorbent is probably not much different.

Table 7 shows the elemental composition of adsorbents from EDX analysis. Information from this analysis represents only the composition on the adsorbent surface. Carbon content of sludge decreased after activation with nitric acid impregnation and carbonization. This carbon composition represented of carboxyl groups within the adsorbent (Jungtiyanont, 2003). The high amount of oxygen on adsorbent surface attributed to the rich in surface oxygen functionalities and/or oxides. It indicated that oxide material was high potential for adsorption especially the highest oxygen level of NS which added in activation with nitric acid. On the other hand, the amount of oxygen in CS and CNS was decreased between activation with carbonization because carbonization process results in the decline of oxygen and carbon (Smith *et al*., 2009).

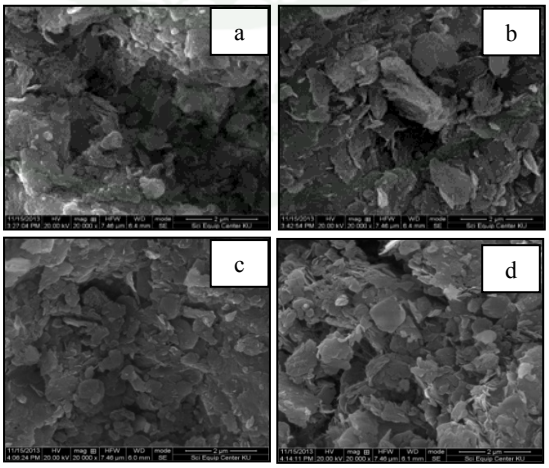


Figure 13 Surface morphology of (a) S, (b) NS, (c) CS and (d) CNS at 2000x

Table 7 Elemental analysis of sludge-adsorbents

Element	Weight%			
	S	**NS**	**CS**	**CNS**
C	54.81	33.44	35.19	38.78
O	29.09	33.6	19.89	20.03
Mg	0.22	0.4	0.5	0.88
Al	3.86	7.1	11.49	11.54
Si	8.11	18.84	22.68	18.72
K	0.57	0.97	2.33	1.97
Ca	0.24	0.12	0.59	0.56
Ti	0.19	0.47	0.47	1.15
Mn	0.11	0.33	0.43	0.93
Fe	2.13	3.29	4.98	3.93
Sr	0.2	0.8	0.85	0.88
Tl	0.47	0.64	0.6	0.63
Total	100	100	100	100

1.2 BET-N_2 surface

Nitrogen adsorption/desorption isotherm curve of S, NS, CS and CNS at 77 K were shown in Figure 14. International Union of Pure and Applied Chemistry (IUPAC) suggested that isotherms are a type II adsorption/desorption isotherm. This isotherm type corresponds with monolayer adsorption, and the most of porosity was mesoporous (Liu *et al*., 2013). BET surface area, total pore volume, and average pore diameter of sludge-adsorbents were shown in Table 8. Generally, BET surface area and the total pore volume increased while the average pore diameter decreased when S was modified with nitric acid and carbonization (NS, CS and CNS). To compare and hypothesize the result after MB adsorption, all sludge-adsorbents except unmodified sludge (S) showed the higher BET surface area. The higher total pore volume and the smaller average pore diameter indicated better adsorption efficiency and catalyst capacity for Fenton-like process. BET surface area of carbonized modified sludge increased due to an increasing of aromatization that occurred at high

temperature. In addition, water releasing in dehydroxylation could aid pore formation (Smith *et al*., 2009). Carbonization increased surface area and pore volume through unblocking of volatile organic matter in sludge, this means fully carbonization the organic matter (Bagreev *et al*., 2001). After carbonization, HCl washing affect to increasing of surface area. It is described by Ros *et al*. (2006) that this increase resulted in organic and inorganic removal and improvement in the accessibility of the carbon fraction. This corresponds with results of CNS. All sludge-adsorbents were found to be highly mesoporous, average pore diameter width in range 6-13 nm, which was practically suitable to remove medium molecule size of methylene blue (1.4 nm) from aqueous solution (Dogan *et al*., 2007).

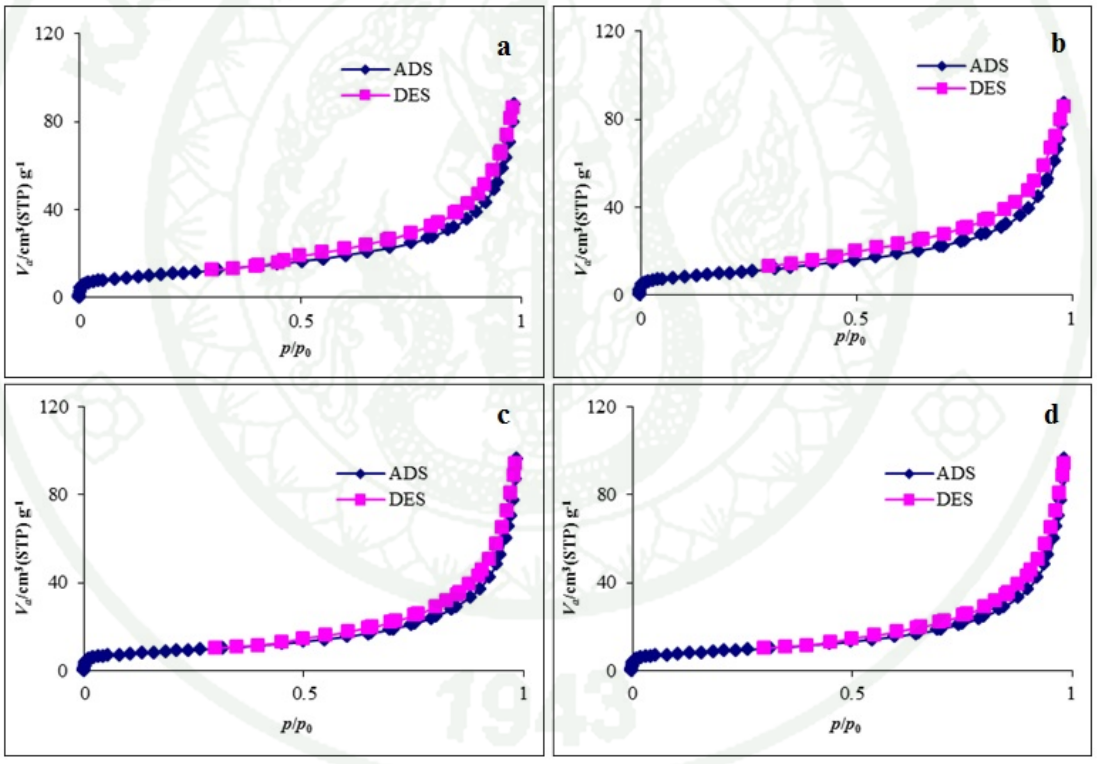


Figure 14 Nitrogen adsorption/desorption isotherm at 77 K of all adsorbents by nitrogen; (a) S (b) NS (c) CS (d) CNS

Table 8 BET results of sludge-adsorbents

Type	S	NS	CS	CNS
BET surface area (m^2/g)	33.98±4.88	58.26±0.27	47.65±1.34	63.70±1.52
Total pore volume (cm^3/g)	0.06±0.05	0.12±0.09	0.11±0.07	0.14±0.01
Average pore diameter (nm)	12.96±7.69	6.56±5.50	7.39±5.30	6.05±0.06

1.3 Fourier transforms infrared spectroscopy analysis (FTIR)

FTIR spectra and the respective assignments of modified and unmodified sludge were given in Figure 15 and Table 9. S and NS showed a common broad peak centered between 3696 and 3556 cm^{-1} which indicated the presence of –OH stretching in bonded. CS and CNS did not exist in the wavelength of –OH functional group. This functional group was likely potential to participate in MB adsorption. A well-known mechanism involved in the adsorbate and adsorbent interaction was controlled by ion exchange process and followed by the adsorption process (Junlaoun, 2007). In the adsorption process, leaving OH^- ion of the adsorbent bound with MB ion at the adsorbent surface due to electrostatic attraction (Jungtiyanont, 2003). The second peaks observed at 1016-996 cm^{-1} of sludge-adsorbents could be assigned to the C-O stretching of alkenes. In addition, the third peaks are at 796-777 cm^{-1}, indicating the presence of =C-H bending of alkenes groups. From above results, S and NS were relatively abundant in hydroxyl functional groups than CS and CNS. It was also useful to observe that CS and CNS were produced with heating open-air system (carbonization), in which most of –OH functional groups were liberated and removed during the modification. Therefore, the MB adsorption of S and NS was more effective than the adsorption with CS and CNS.

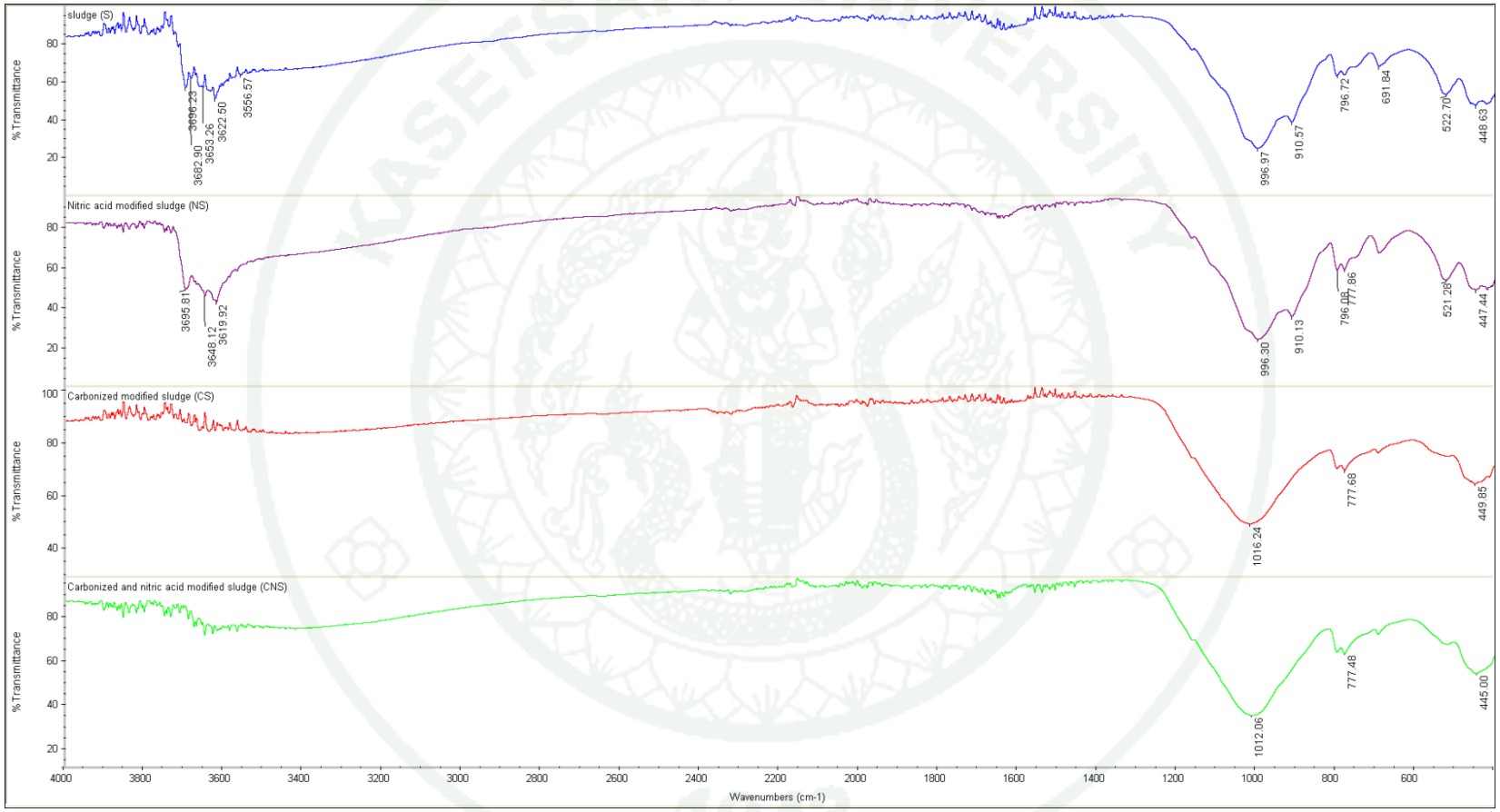


Figure 15 FTIR spectra of S (a) NS (b) CS (c) and CNS (d)

Table 9 FTIR assignment of sludge-adsorbent

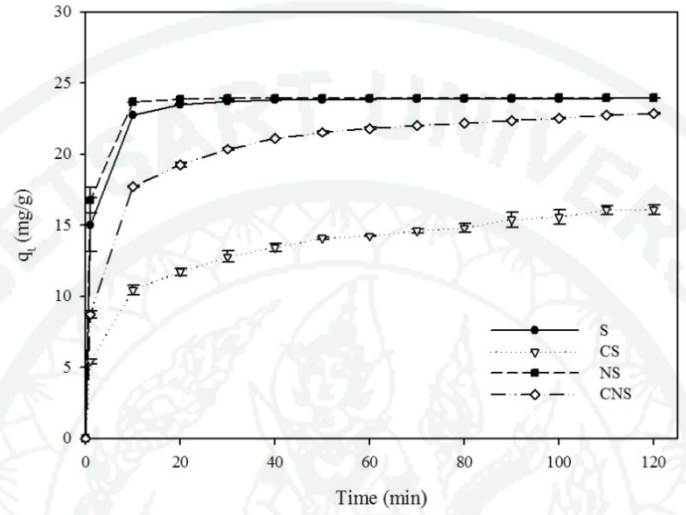
Wavelength (cm^{-1})				Assignment
S	**NS**	**CS**	**CNS**	
3696-3556	3695-3619	-	-	O-H stretch (Alcohol)
996	996	1016	1012	C-O stretch (Alkenes)
796.72	796.08	777.68	777.48	=C-H bending (Alkenes)

2. Preliminary test for material selecting

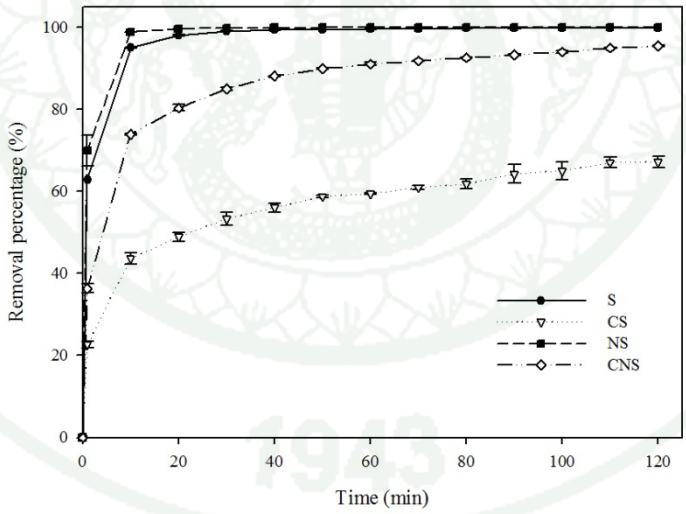
The experiment was conducted at MB concentration 100 mg/L stirring speed 400 rpm, room temperature, adsorbent dose of 1 g/200 ml (5g/L) in unbuffered MB solution. Figure 16 shows that S and NS exhibited the higher effective than CS and CNS in MB adsorption at 100 mg/L. The removal percentage of MB by S and NS was 99.86 and 100, respectively. The amount of adsorbed MB on S and NS was 23.92 and 23.96, respectively. The higher adsorption efficiency of the unmodified sludge (S) and nitric acid modified sludge (NS) could be attributed to the presence of organic matter and OH- functional group on the sludge. OH- functional group on surface of S and NS was responsible for attracting positively charge of MB whereas CS and CNS did not have OH- functional group on the surface (Figure 15 and Table 9). When sludge was modified at 700^0C, OH- and volatile organic matters were removed, resulting in decreasing of active site at surface for adsorption. This result corresponded with results from EDXs and FT-IR analysis. Hence, S and NS were selected as material for further study in dye adsorption.

After material selecting, the selected adsorbents were analyzed surface charge by zeta potential measurement. Zeta potential measurement was investigated using Malvern zetasizer by salt addition method. 50 ml of 0.1 M NaCl solutions was taken into the different flask. The pH of the solution was adjusted to 2, 4, 6, 8, 10, and 12 by 0.1M HCl and NaOH solutions. According to zeta potential measurement of S and NS

(Figure 17), the results indicated that negative charges of S and NS surfaces occur in pH range from 2-12. It suggested that the adsorbent materials have a potential to attract positively charged molecule of a cationic dye (MB). This result corresponded to using montmorillonite in MB adsorption (Almeida *et al.*, 2009).



(a)



(b)

Figure 16 The amount of adsorbed MB on sludge-adsorbents (a) and removal percentage (b) at 100 mg/L, stirring speed 400 rpm, room temperature, adsorbent dose of 1 g/200 ml (5g/L) in unbuffered MB solution

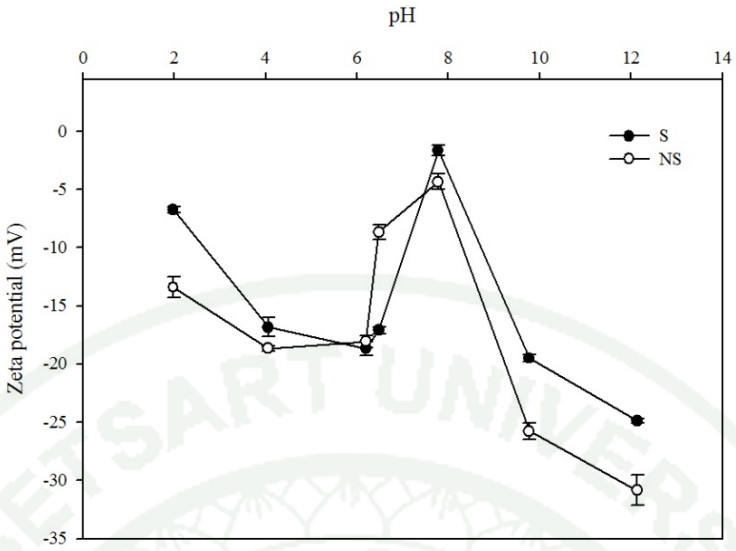


Figure 17 Zeta potential of S and NS from pH 2-12

3. Effect of initial MB concentration

The initial concentration of adsorbate solution is important factor in driving and attractive force between liquid of adsorbate and solid phase of adsorbent to conquer mass transfer resistance (Garg *et al*., 2004). Experiment was carried out with various initial MB concentration in the presence 1 g of adsorbent and 200 mL of unbuffered MB solution. This study was investigated by varying MB concentration in range of 100-1000 mg/L. Figure 18 shows that the q_e of S and NS increased with the increasing of the initial MB concentration from 100 to 1000 mg/L due to concentration gradient between adsorbate and adsorbent surface, and high mass transfer force at high MB concentration. Effect of initial concentration was shown in Figure 19 and Appendix B. The removal percentage of MB was inversely different. The removal percentage decreased when the MB concentration increased. At higher concentration, MB was not completely adsorbed onto S and NS because of the saturation of adsorbent material thus remaining MB in solution. In addition, the concentration gradient is reduced due to accumulation of MB on the active site of adsorbent leading to decreasing adsorption rate at the latter stage of adsorption. The higher adsorption rate at initial period of each MB concentration may be due to high available active site that make more intense of concentration gradient between

adsorbate and adsorbent (Rodriquez *et al.*, 2009). The highest efficiency of MB removal was at 100 mg/L (the lowest concentration). The results indicated that removal efficiency of NS was higher than that of S due to higher surface area and total pore volume (Table 8). The similar results have been reported in dye removal by using montmorillonite, activated carbon, and teak tree powder (Almeida *et al.*, 2009; Rodriquez *et al.*; Patil *et al.*, 2011).

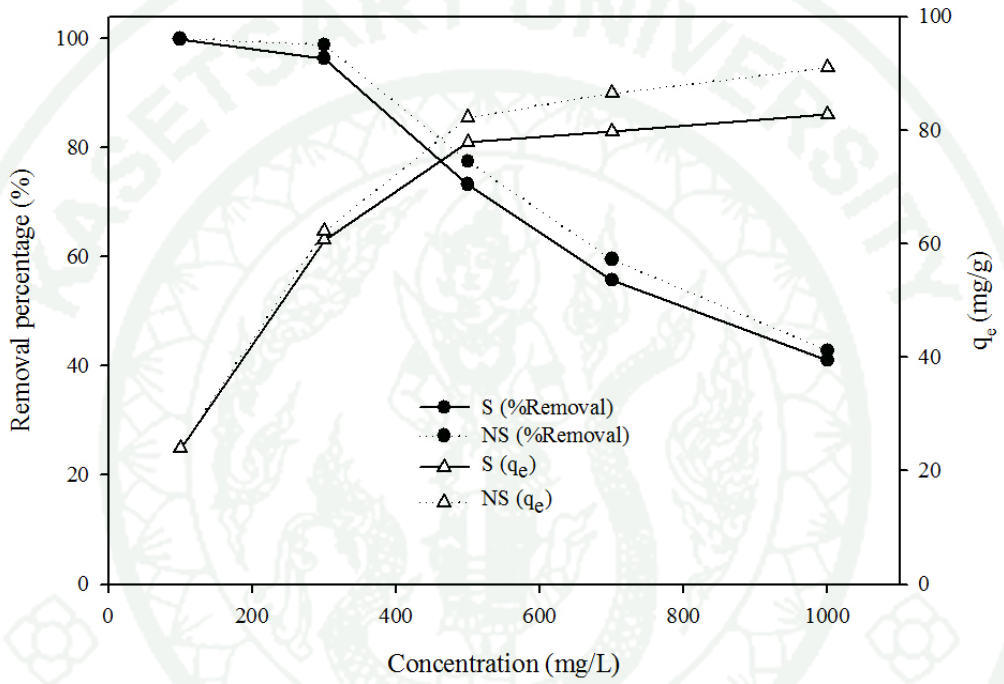
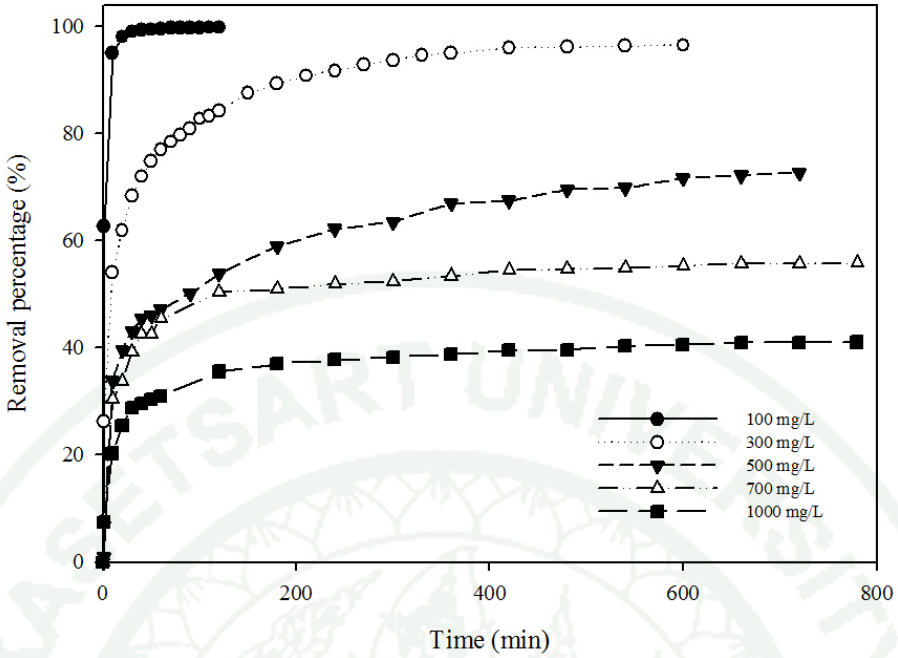
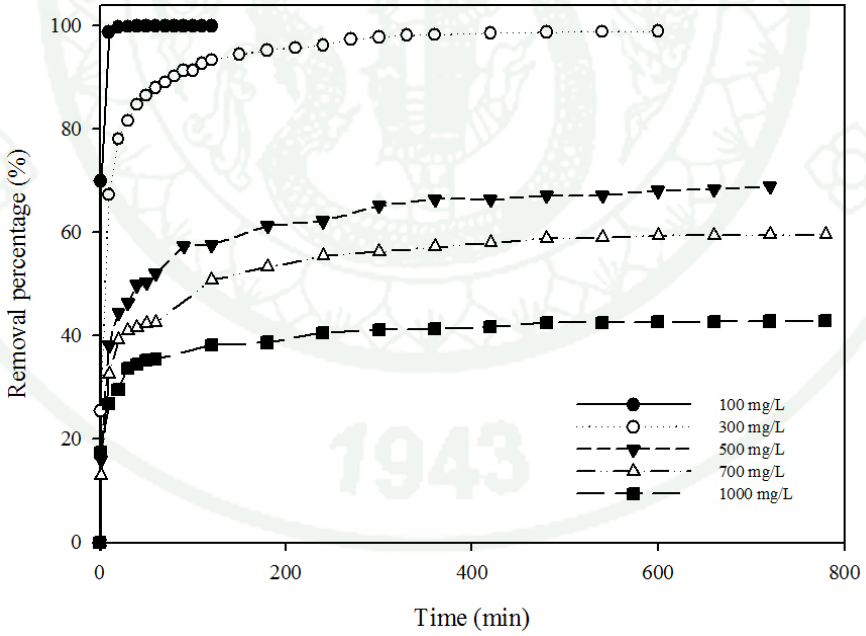


Figure 18 The effect of initial MB concentration on adsorption process; removal percentage and the amount of MB adsorbed per unit mass of adsorbent at equilibrium time (q_e)



(a)



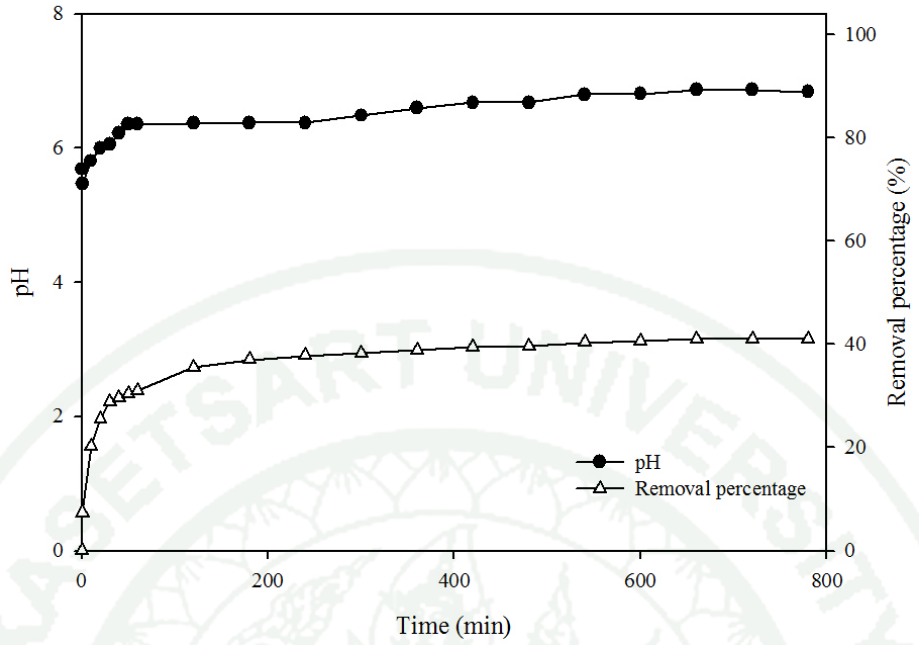
(b)

Figure 19 Effect of initial MB concentration onto S (a) and NS (b)

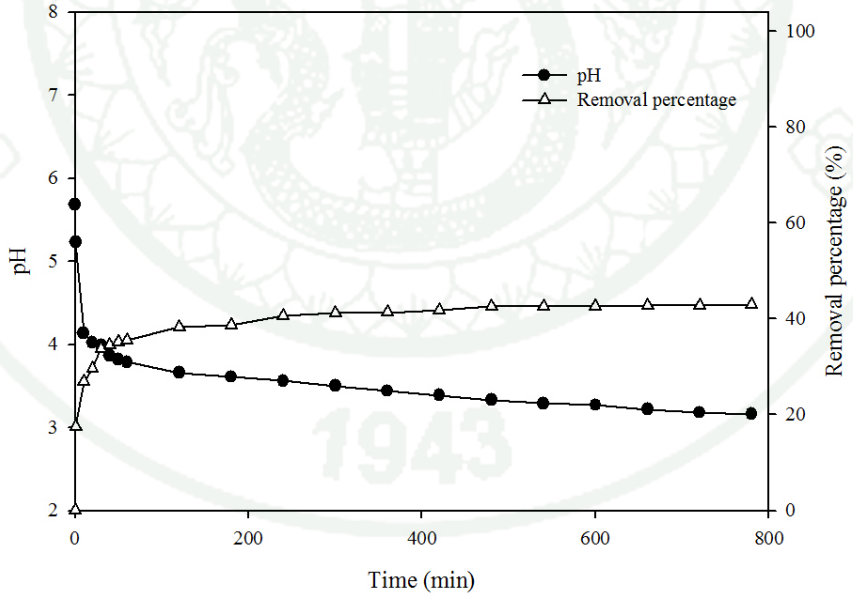
4. Effect of initial pH solution

Several researches explained that pH is an important factor in controlling adsorption process. Therefore, the experiment was carried out to study effect of initial pH solution (in range pH 2-11) in MB adsorption on S and NS. This work used best condition from studying of initial MB concentration (1000 mg/L) because it showed the highest amount of MB adsorbed onto S and NS. The effect of pH is shown in Figure 20a and 20b. Under natural pH of MB solution with unbuffered condition, the pH of solution was decreased by the time after adding NS, on the other hand adding S in MB solution affect in increasing of pH solution. After sludge modification with nitric acid, sludge was protonated and this cause releasing proton into solution when adding NS which was observed by pH measurement. This result illustrated that the adsorbent affects to pH of solution.

The results indicated that the adsorption of MB was increased with increase in pH (Figure 21a and 21b). The maximum removal was observed at pH 11. At acidic and alkaline solution, the hydrogen ion (H^+) and hydroxyl ion (OH^-), respectively were strongly and rapidly adsorbed on adsorbent; therefore, adsorption of other ion was affected by pH of solution. Functional group on the adsorbent surface can be also affected when pH solution change (Patil *et al.*, 2011). Increasing of pH solution increased the number of hydroxyl groups thus, increased the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface. Therefore, as pH was increased, the functional groups on adsorbent surface were deprotonated, which results in a decrease in surface charge density. This implies that the adsorption of cationic dye could be enhanced at higher pH (Baybars *et al.*, 2012; Martin *et al.*, 2003).

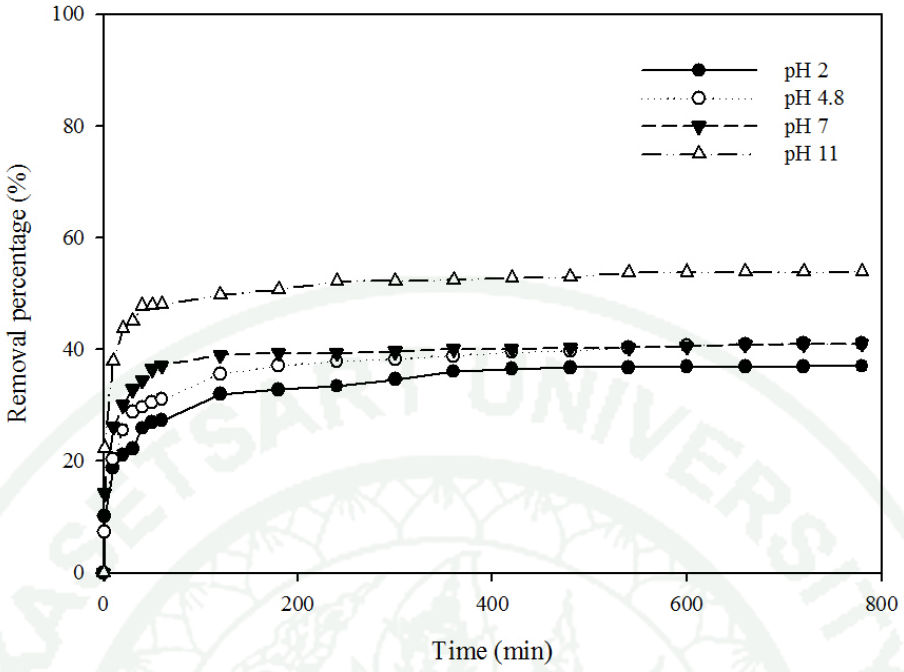


(a)

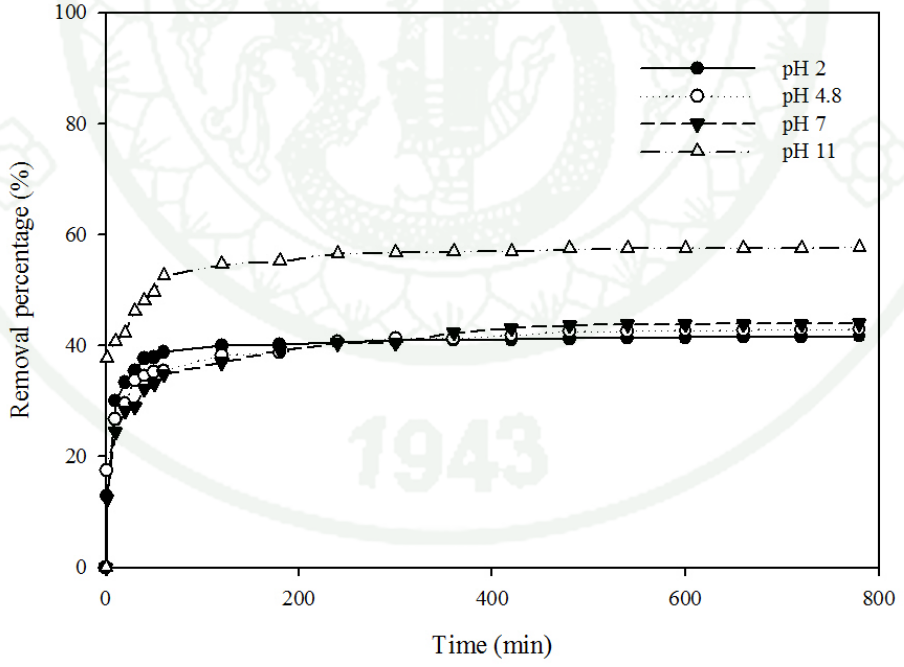


(b)

Figure 20 The effect of natural pH of MB solution with unbuffered condition after adding S (a) and NS (b)



(a)



(b)

Figure 21 The effect of pH in MB removal using S (a) and NS (b)

Usually, the cationic dye (MB) expresses as a positively charge when dissolved in water. As in acidic condition, the positively charged surface of adsorbent tended to resist adsorption of cationic group due to the presence of excess H^+ ions competing with cation of MB for adsorption sites on adsorbent. In addition, the electrostatic repulsion between MB ions and positive charge ($SiOH_2^+$) on the adsorbent occurred in acidic condition as following.

$$\text{-SiOH} + H^+ \longrightarrow \text{-SiOH}_2^+ + OH^- \quad (22)$$

When pH of solution was increased, the surface of adsorbent tended to obtain the negatively charge and decrease electrostatic repulsion. Thus, it resulted in MB adsorption increase because of attractive force between negatively charge surface of adsorbent and positively charge of MB (Baybars *et al*., 2012). This mechanism was shown by following equation.

$$\text{-SiOH} + OH^- \longrightarrow \text{-SiO}^- + H_2O \quad (23)$$

$$\text{SiOH} + MB^+ \longrightarrow \text{-Si-O-MB}^+ \quad (24)$$

5. Adsorption isotherm and kinetic

5.1 Adsorption isotherm

Adsorption isotherm was carried out with Langmuir and Freundlich adsorption isotherm equation. The Langmuir and Freundlich isotherms were used to fit the adsorption data. Both isotherm models were shown as Equation 5 and 7, respectively. Langmuir isotherm assumes that surface of the adsorbent is uniform, and adsorbate molecules adsorbed on the adsorbent is monolayer. The adsorbate molecules do not interact with other adsorption sites. Freundlich isotherm assumes heterogeneous surface energies. It will give exact result when the adsorption is clearly physical process without any change in the adsorbed state (Nokkaew, 2008).

MB adsorption data were plotted in Figure 22a and 22b. According to linear correlation coefficient (R^2), it confirmed that the adsorption data of S and NS were fit well with Langmuir isotherm more than Freundlich isotherm (Table 10). This result indicated that MB adsorption onto S and NS are monolayer adsorption. Therefore, it should be pointed out that MB adsorption was caused by the interaction between positively charged group of MB and negatively charge group (-OH) via electrostatic attraction force which was observed in FTIR results and Equation 24. The maximum capacity (Q_o) of NS obtained from Langmuir isotherm was higher than S but an adsorption rate (b) of S is faster than NS. This tendency is reasonable since the adsorption affinity and monolayer adsorption capacity were enhanced with increasing surface area of NS adsorbent which were observed in Table 8. The important factor of Langmuir model can be described in term of a dimensionless separation factor (R_L) which is defined as $R_L = 1 / (1+bC_o)$. It suggests that type of isotherm is irreversible ($R_L = 0$), favorable ($0< R_L<1$), linear ($R_L = 1$), and unfavorable ($R_L>1$).

Figure 23 shows the R_L profile of S and NS. As can be seen, these adsorbents display the R_L values ranging from 0.005 to 0.056; conformed to the favorable of adsorption at all initial concentration of MB. However, the R_L values of S were lower than NS at every initial concentration, illustrating that they were more favorable in adsorption. The R_L values closing zero at higher initial concentration also indicated a higher intensity of MB adsorption. The similar results have been reported in dye removal by using activated carbon (Martin *et al*., 2003).

Table 10 The adsorption parameter of Langmuir and Freundlich isotherm

Adsorbent	Langmuir isotherm				Freundlich isotherm		
	Q_o (mg/g)	b (L/mg)	R^2	R_L	K_F (L/g)	1/n	R^2
S	82.6446	0.183	0.9995	0.0054-0.0518	34.5701	0.1528	0.9443
NS	90.9091	0.168	0.9991	0.0059-0.0561	50.5359	0.0985	0.9918

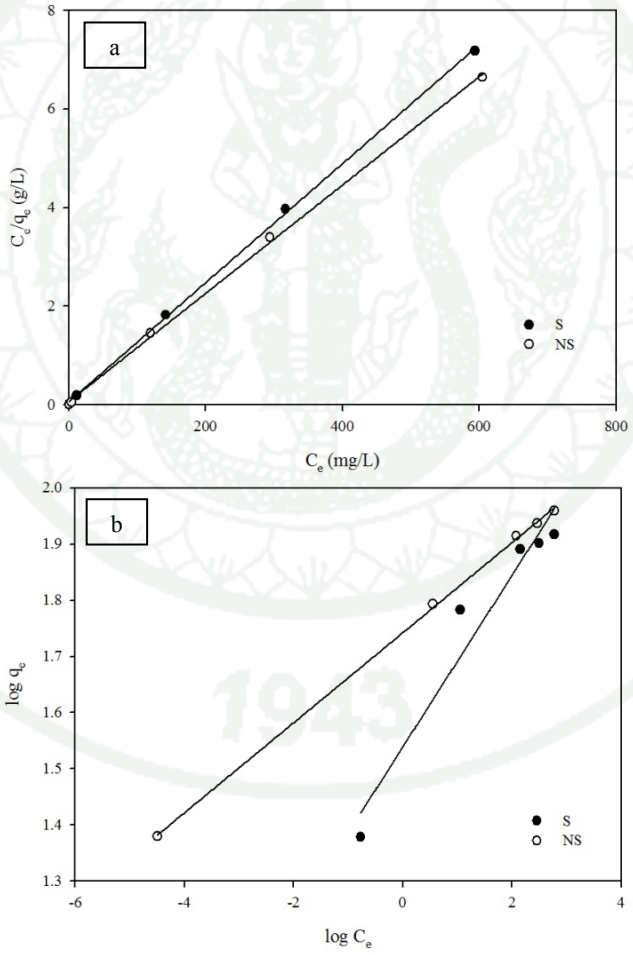


Figure 22 Adsorption isotherm of sludge-adsorbent for MB adsorption; (a) Langmuir isotherm (b) Freundlich isotherm

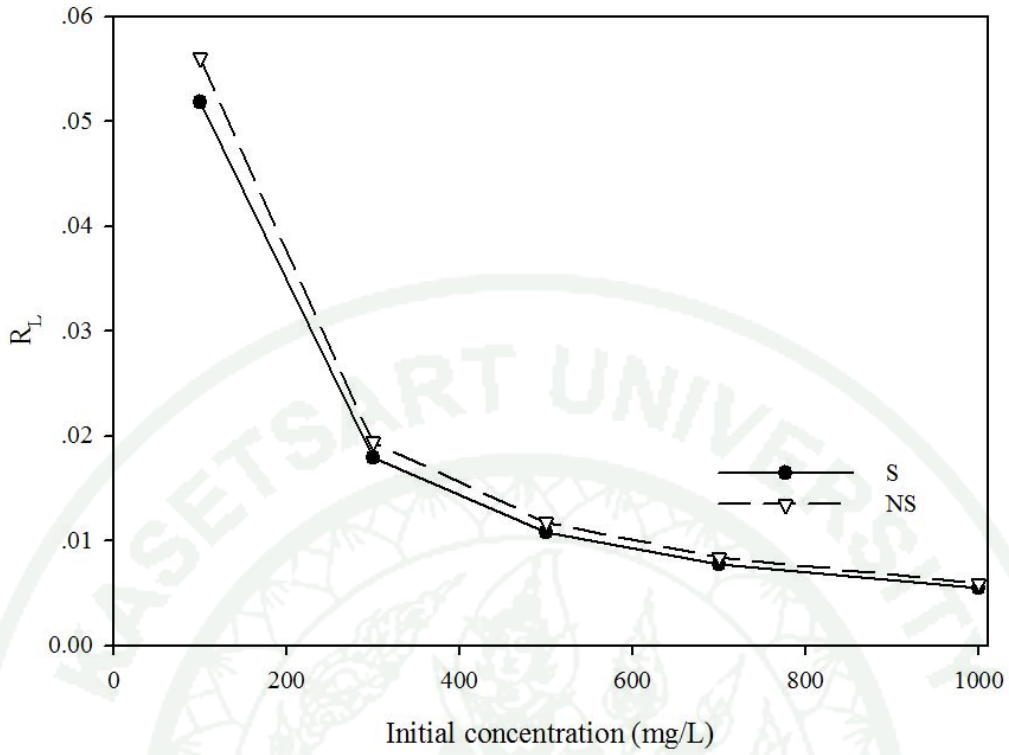


Figure 23 Langmuir separation factor (R_L)

Table 11 summarized MB removal by various adsorbents. It noted that the adsorption capacity for MB onto S and NS was higher than other adsorbent due to higher surface area excepting with $ZnCl_2$-activated coconut coir dust. This table indicated that the adsorption was sensitive to surface area, pore textures. In this study, sludge-adsorbents from water treatment plant showed a comparative result of MB removal with other adsorbents which reported in literature.

Table 11 Comparison of the adsorption capacities of MB by different adsorbents

Adsorbent	Adsorption capacity (mg/g)	Surface Area (m^2/g)	Reference
Anaerobic granular sludge	45	-	Liu *et al.* (2013)
Sugar extracted spent rich biomass	8.13	0.41	Kim *et al.* (2012)
Sepiolite	67.30	-	Dogan *et al.* (2007)
NaOH-treated waste activated sludge	53.7	67	Gobi *et al.* (2011)
$ZnCl_2$-activated coconut coir dust	14.4	1884	Macedo *et al.* (2006)
Fly ash treated with HNO_3	7.10	-	Wang *et al.* (2004)
Natural Jordanian Tripoli	9.76	46.5	Alzaydien (2009)
Unmodified sludge	82.64	33.98	This study
HNO_3-modified sludge	90.91	58.26	This study

5.2 Adsorption kinetic

It is important to be able to predict the mechanism and rate at which pollutant is removed from aqueous solutions in order to design the adsorption process in treatment plant. As seen in Figure 19 and 21, the adsorption process were quite rapid and most of the MB were adsorbed within the first of 60 min of contact with sludge-adsorbent. To investigate and understand about adsorption process of MB on sludge-adsorbent (S and NS), pseudo-first-order and pseudo-second-order models were applied to fit the adsorption data.

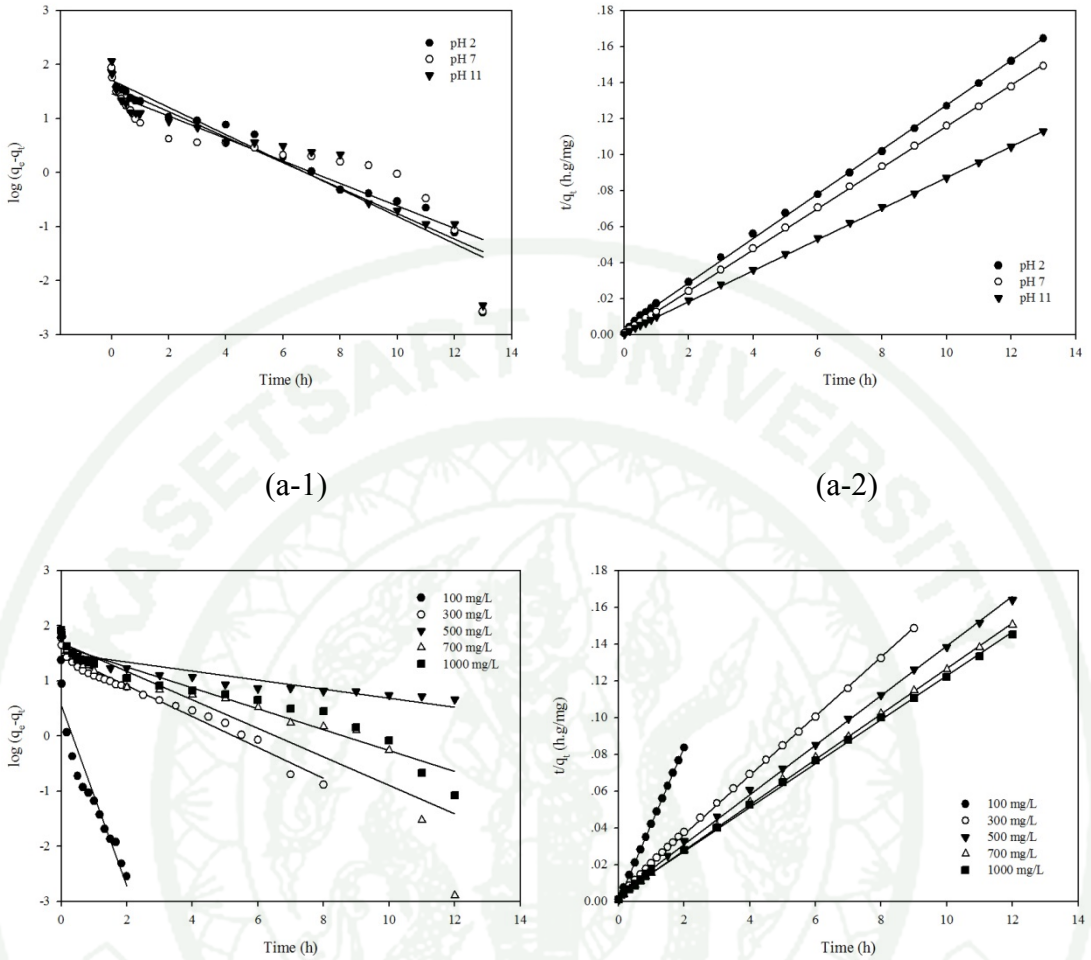


Figure 24 Kinetic model of MB adsorption onto S: (a) initial pH; (b) initial MB concentration; (1) pseudo first order model (2) pseudo second order model

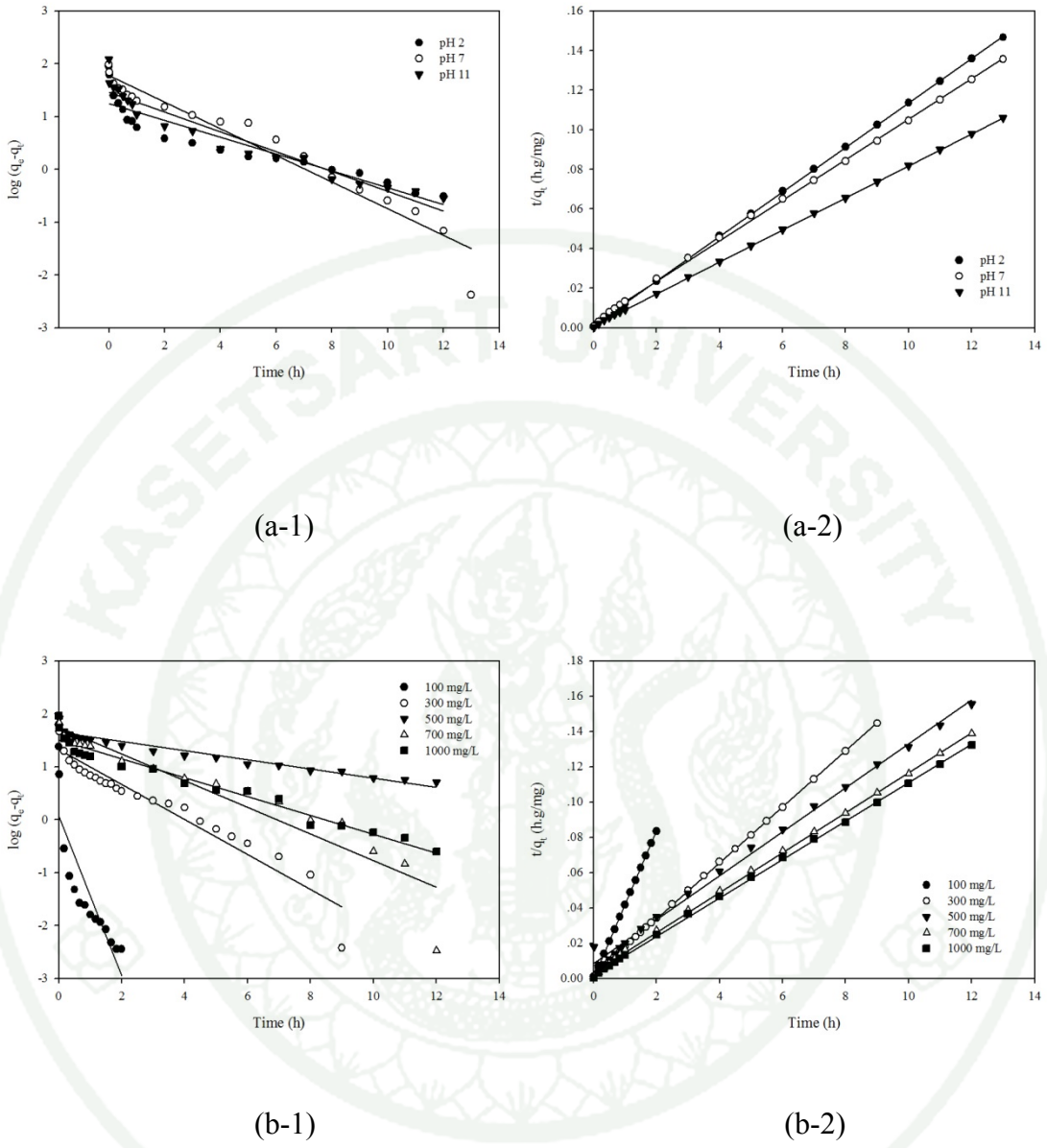


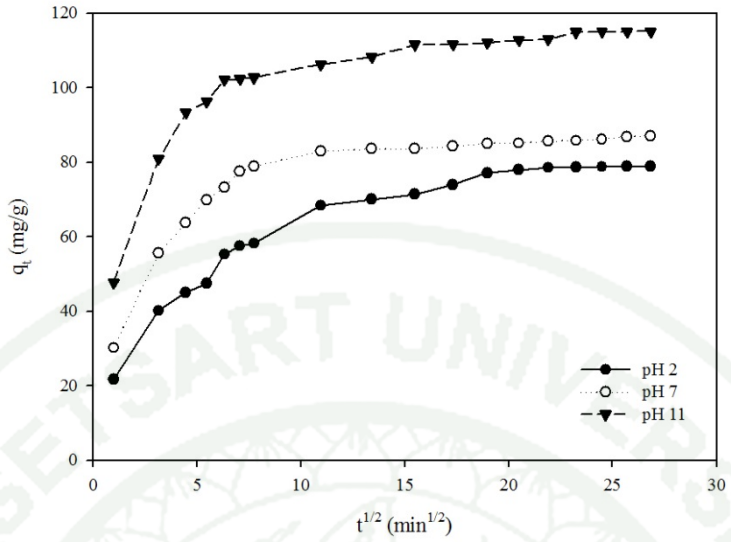
Figure 25 Kinetic model of MB adsorption onto NS: (a) initial pH; (b) initial MB concentration; (1) pseudo first order model (2) pseudo second order model

Figure 24 and 25 show the plots of t/q_t versus t for the data of Figure 19 and 21. Calculated correlation coefficients (R^2) and related parameter for pseudo-first-order and pseudo-second-order models of MB adsorption onto S and NS were shown in Appendix B. For correlation coefficients of pseudo-second-order is closer to unity more than correlation coefficients of pseudo-first-order, this indicated that adsorption

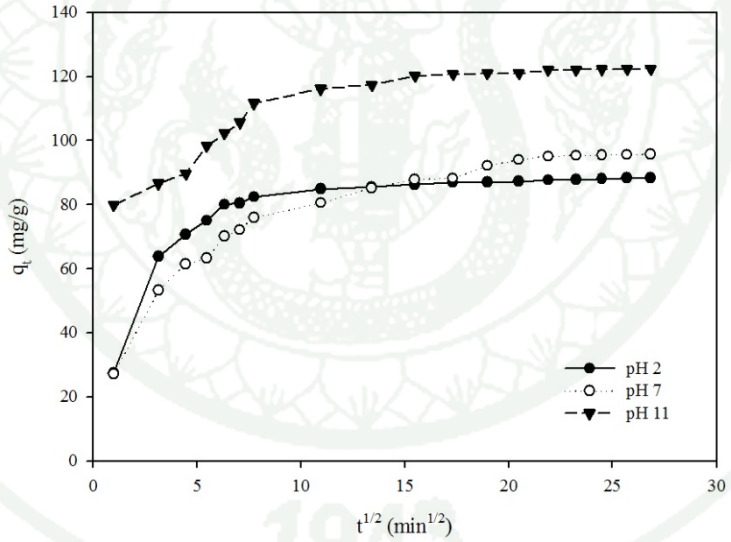
data fit well with pseudo-second-order kinetic model. Another reason of adsorption data fit well with pseudo-second-order kinetic model, the values of $q_{e,cal}$ in pseudo first order model failed to predicate the values of $q_{e,exp}$ while the value of $q_{e,cal}$ in pseudo second order model was pretty close to $q_{e,exp}$. These evidences confirmed MB adsorption onto S and NS follow pseudo second order kinetic model. The value of k_2 showed the rate of adsorption process that if the higher k_2 was faster reaction than the lower k_2. Similar results have been observed in the dye adsorption on natural tripoli, activated carbon and montmorillonite clay (Alzaydien, 2009; Rodriguez *et al*., 2009; Almeida *et al*., 2009).

According to the results of kinetic model, the applicability of pseudo second order model suggests that the adsorption of MB onto S and NS is a chemisorption process. The chemisorption process involves valence force through sharing or the exchange of electron between adsorbent surface (sludge) and adsorbate (MB) as covalent forces (Dogan *et al*., 2004). MB was classified to be an organic substance and basic dye and MB in solution is express as positively charge. Water treatment sludge is a metal oxides-base and the surface of metal oxide in contact with water is shown negatively charge, thus it is likely that a chemical reaction may be taking place. This corresponds with the result from kinetic test. Although NS was effective than S, the values of $t^{1/2}$ of S was higher than NS in all parameter. It indicated that adsorption of S take time less than NS at same condition.

If the intra-particle diffusion is involved in the adsorption process, then the plot of the square root of time ($t^{1/2}$) versus the uptake (q_t) would result in a linear relationship. The dependencies of $t^{1/2}$ versus q_t are shown in Figure 26. The results showed that the plot of S and NS presented a multilinearity, which indicated that two or more steps occur in the adsorption process. These multilinearity plots have been reported similarly in other works, for example, dye adsorption on sawdust (Garg *et al*., 2004), perlite (Dogan *et al*., 2004) and sepiolite (Dogan *et al*., 2007).



(a)



(b)

Figure 26 Intra-particle diffusion plots for different initial pH of solution: (a) S and (b) NS

The two linear sections were separately investigated using Equation 12, and the intra-particle diffusion parameters were reported in Table 12. The first straight portion was attributed to the macro pore diffusion (stage 1). Stage 1 was the fastest

and completed within 15 min. This was attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The second portion linear portion (stage 2) to micro pore diffusion was stage of intra-particle diffusion control. It was attained and continued from 15-120 min. Finally, final equilibrium adsorption (stage 3) took place after 120 min. Both stage 2 and 3 may be attributed to a very slow diffusion of the adsorbate (MB) from the surface film into micro pore which were the least accessible sites of adsorption. Also, this stimulated a very slow rate of migration of adsorbate from the liquid phase on to the adsorbent surface and it corresponded to the $k_{id,2}$ values less than the $k_{id,1}$ values of both S and NS (Dogan *et al*., 2007; Zaini *et al*., 2013).

Table 12 Intra-particle diffusion parameter of S and NS

pH	$k_{id,1}$	C_1	R_1^2	$k_{id,2}$	C_2	R_2^2
Unmodified sludge (S)						
2	5.3456	19.555	0.9608	0.2614	61.096	0.8922
7	7.0172	28.8040	0.9472	0.5338	79.906	0.9815
11	7.8886	49.68	0.8743	0.7333	101.74	0.9206
Nitric acid modified sludge (NS)						
2	4.6977	30.412	0.8599	0.218	82.757	0.9681
7	6.7725	26.3400	0.9369	0.3731	72.366	0.9101
11	7.5772	72.65	0.9609	0.9564	113.29	0.8502

However, these plots did not pass the origin, indicating intra-particle diffusion was involved in the adsorption process but it was not the only rate limiting mechanism and that some other mechanisms also play an important role. Surface adsorption and intra-particle diffusion were likely to take place simultaneously, both the processes controlling the kinetics of dye-adsorbent interaction. Value of intercept (C_1 and C_2) gave idea about the thickness of boundary layer. Value of C_1 in this plot was less than C_2, indicating reaction rate of stage 1 faster than stage 2 because of less of boundary layer (Alzaydien, 2009).

6. Effect of Fenton-like process on MB removal

Among advanced oxidation process, the oxidation using Fenton's reagent as proved to be a promising and attractive treatment method for the effective decolorization and degradation of dyes. Fenton-like reactions can eliminate pollutants efficiently in a wider pH range. In experiment, adsorption process was carried out before Fenton-like process occurred. Hydrogen peroxide (30% w/w) was added after 30 min of adsorption process to form Fenton reagent with Fe in sludge. The experiment was conducted at highest initial MB concentration (1000 mg/L) in order to improve the efficiency in MB removal by adsorption combined Fenton-like process. The result in MB removal was shown in Figure 27. After 30 min, the removal percentage by adsorption with Fenton-like process on NS was rapidly increased from 36.42% to 80.52% within 10 minutes. At equilibrium time, removal percentage of S and NS in adsorption process was 41.02 and 42.82, respectively. However, adsorption combined with Fenton-like process of S and NS was 48.89 and 99.96, respectively. Adsorption with Fenton reagent of S was not different from adsorption process of S and NS, but that of NS shows highly different removal percentage. This corresponded with TOC results which are one of crucial parameters for wastewater treatment. TOC analysis showed oxidation that leads to the conversion of organic compounds into harmless gaseous CO_2 and inorganic ions (Punizi *et al.*, 2012). TOC value for MB removal by NS with Fenton-like reaction exhibited less than S with Fenton-like reaction (Figure 28). Mentioned evidences confirmed that MB was oxidized into carbon dioxide, and transformation of MB by NS had more removal efficiency.

MB removal was caused by degradation of Fenton-like process which was done well under low pH (pH 3-4). Fenton-like processes involve the reaction of hydrogen peroxide with ferrous (Fe^{2+}) and ferric (Fe^{3+}) ion, respectively. Iron species in water treatment sludge play a critical role in catalytic activity of MB removal via oxidation process. They could catalyze the activation of H_2O_2 to produce hydroxyl ($HO^{\bullet}$) and perhydroxyl ($HO_2^{\bullet}$) radicals (Equation 19 and 20). Beside iron species, the catalytic phase of sludge can also have its origin in other inorganic matter. Sludge consists of mixtures of silica, alumina and calcium (Table 7). Those species are known as catalysts of many oxidation reactions (Gu *et al.*, 2013). Therefore, the best

results from this experiment took place with using NS as adsorbent and catalyst because adding NS cause decreasing of pH in solution, this made favorable condition for degradation by Fenton-like process. This result agreed with literature review, as it was usually accepted that acidic pH level near 3 were appropriate for Fenton and Fenton-like process (Rache *et al*., 2014). Another reason is described by Ramirez *et al*. (2008) that the pH level higher than 3, the stability of hydrogen peroxide was decreased because of formation of hydroxyl radical to be hydroperoxonium ($H_3O_2^+$). It was seen in result of S with Fenton-like process in Figure 27. Figure 29 shows decreasing of pH after adding NS. The comparative study of adsorption and Fenton-like process showed that adsorption with Fenton-like process under low pH had higher efficiency than using only adsorption process.

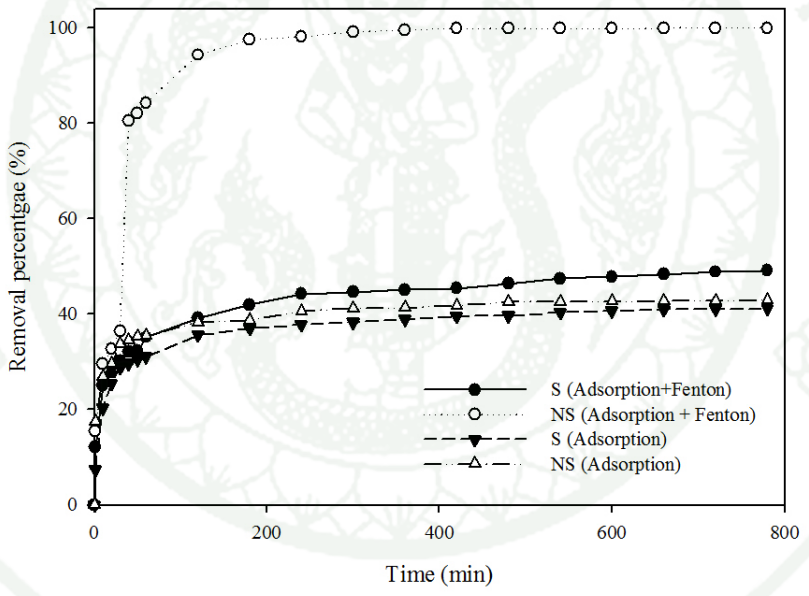


Figure 27 Effect of Fenton-like process on MB removal

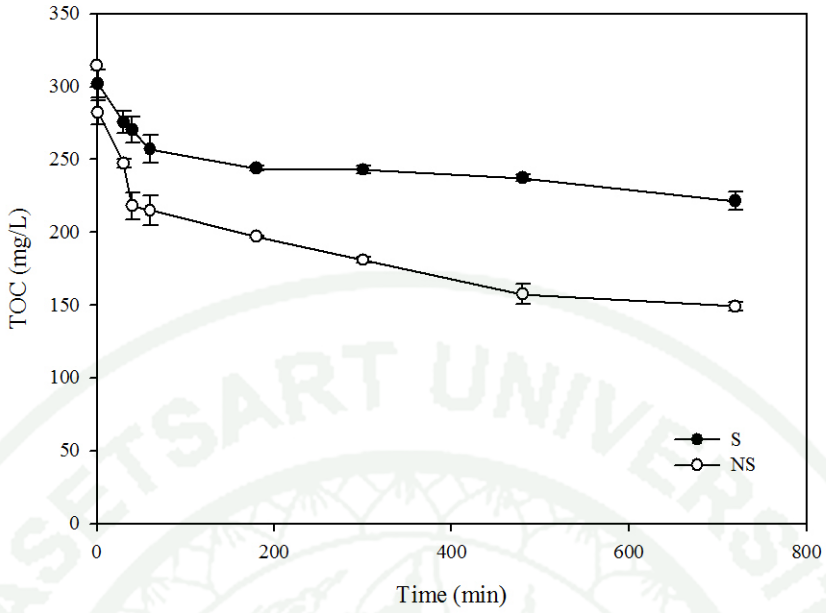


Figure 28 TOC analysis for MB removal

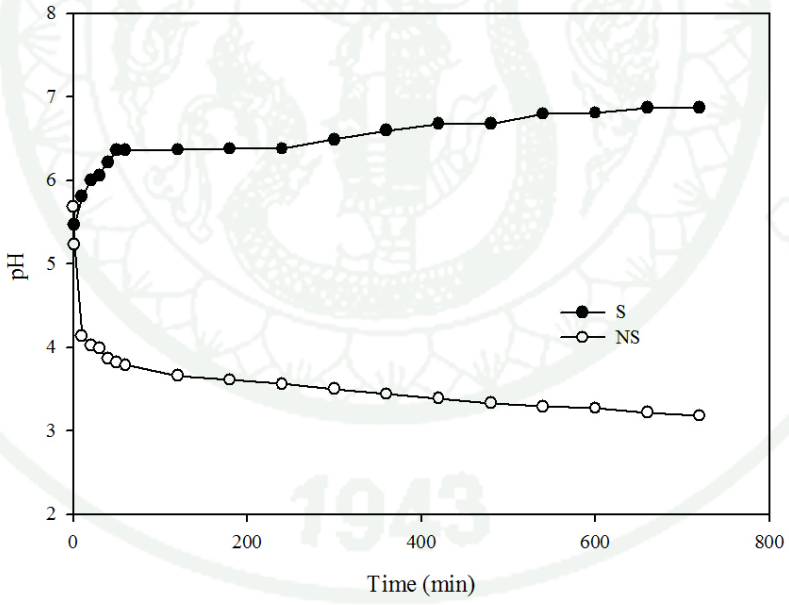


Figure 29 Changing of pH in solution after adding NS and S in adsorption with Fenton-like process

7. Case study: Applying water treatment sludge in K.World Textile industry

Wastewater from the secondary sedimentation tank in K.World Textile Industry is conventionally recycled by adding alum in order to minimize turbidity, flowing through up-down sand filter and adding sodium hypochlorite (NaClO) for disinfection (Appendix D). Even if this recycling process offers a good performance with visualized physical properties, it requires manpower and cost for operation. Therefore, wastewater after the secondary sedimentation tank was treated with sludge which aimed to seeking for alternative treatment method. In addition, this wastewater containing 256 mg/L COD was treated to comply with minimum effluent standard of 120 mg/L COD (Pollution Control Department, 2014).

Textile wastewater experiments of S and NS with and without Fenton-like process were carried out in a batch system. The wastewater was sampled from K.World Textile industry containing 256 mg/L COD. Figure 30 illustrates that using NS with Fenton-like process showed highest COD removal percentage (72.35%) in 12 h. The result showed that adsorption process of S and NS combined with Fenton-like process increased removal percentage. To confirm the synergetic effect of removal efficiency by Fenton-like process, textile wastewater was also treated with only H_2O_2 solution; the results revealed that removal percentage is relatively low with 15.06%. Because Fenton-like process is consisted of H_2O_2 and iron catalyst whereby iron can be found in sludge (Table 7). In addition, iron could not be found in textile wastewater; it consequently explained that wastewater treatment with only H_2O_2 showed low efficiency. Moreover, the results of S and NS with Fenton-like process corresponded with materials characterization that amount of iron in NS was more than S, removal percentage by NS was, thus, higher than that of S. COD values each experiments are shown in Table 13 and the COD result agreed with industrial effluent standards.

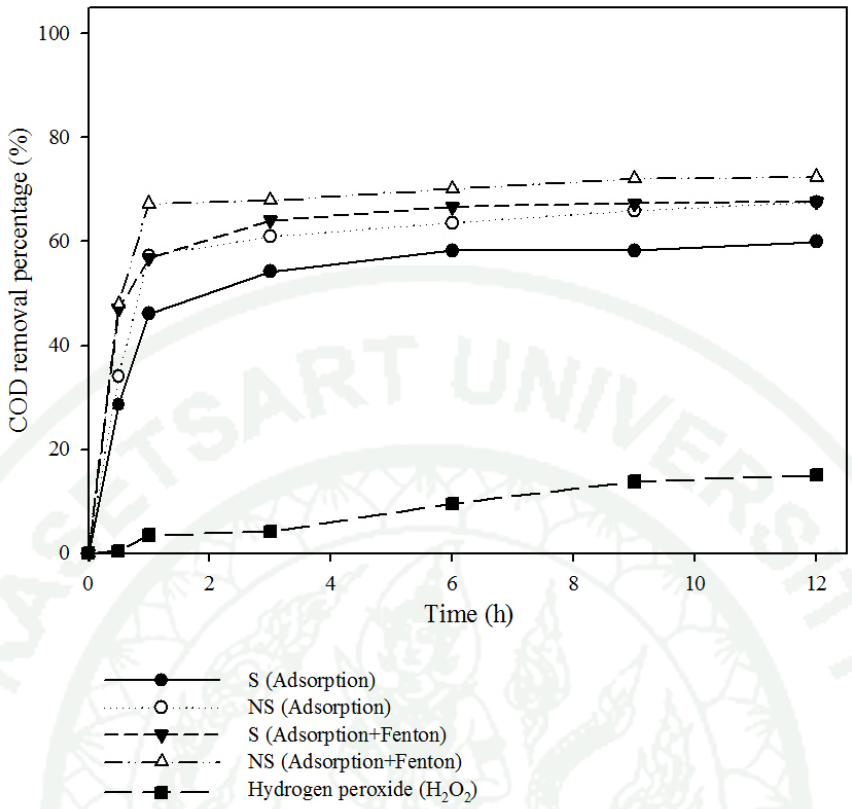


Figure 30 COD removal percentage of textile wastewater in experiment

One of the reasons resulting in higher removal percentage of NS combined with Fenton was lower pH of 3 – 4 which caused from adding NS in wastewater treatment. pH is a crucial parameter for Fenton-like process performance especially acidic condition which accelerates organic degradation due to generation of hydroxyl radical. In addition, the result of textile wastewater treatment corresponded with that of synthetic wastewater experiment (Figure 21).

Cost analysis is a mean to determine the application of waste utilization. Activated carbon has been widely used as an adsorbent in wastewater treatment because of high adsorption capacity. However it was costly, thus several researches have been trying to improve low cost adsorbents in wastewater treatment industry. Table 14 and Appendix C show comparison of material cost (cost operation) between materials in this study and commercial activated carbon. The results illustrated that

cost of unmodified water treatment sludge (S) was lowest but it provided lower efficiency than other materials.

Table 13 COD value after K.World Textile wastewater treatment in 12 h

Treatment process	COD (mg/L)
Unmodified water treatment sludge (S)	119
Nitric acid modified water treatment sludge (NS)	98
Unmodified sludge with H_2O_2 solution (S+Fenton)	99
Nitric sludge with H_2O_2 solution (NS+Fenton)	86

Table 14 Price of material for determining in textile wastewater treatment

Material	Price (baht/kg adsorbent)
Commercial activated carbon	80
Unmodified water treatment sludge (S)	48
Nitric acid modified water treatment sludge (NS)	138
Unmodified sludge with H_2O_2 solution (S+Fenton)	83
Nitric sludge with H_2O_2 solution (NS+Fenton)	173

Adding Fenton-like process into treatment process increased the cost operation but it offered higher removal efficiency than using only adsorption process. Therefore, using unmodified water treatment sludge (S) was an appropriate option for textile wastewater treatment which exhibited low COD in the range of 256 mg/L. For high COD (>1,000 mg/L) values as for the worst case scenario, Fenton-like process with adsorption was a feasible process for treatment because of high removal efficiency. After textile wastewater was treated with all testing materials, the COD value in the wastewater standard was lower than 120 mg/L COD (Table 13) which complied with Wastewater effluent standard (Pollution Control Department, 2014).

CONCLUSION AND RECOMMENDATIONS

Conclusion

In this study, water treatment sludge obtained from Bangkhen water treatment plant were used as an adsorbent for dye removal in synthetic and authentic wastewater. Water treatment sludge was modified with different method; impregnation with nitric acid and carbonization. This study was conducted at 100 mg/L MB for all of sludge-adsorbents to select for the further study. Unmodified and nitric acid modified sludge (S and NS) were selected for the further study because of higher MB removal percentage than carbonized and nitric acid modified sludge (CS and CNS). The removal percentage of MB adsorption onto S and NS was 99.86 and 100, respectively. S and NS were not significantly different in methylene blue removal due to similar zeta potential and hydroxyl functional group on an adsorbent surface. In the adsorption process, the hydroxyl functional group of adsorbent bound with dye ion at the adsorbent surface due to electrostatic attraction including negative charge on adsorbent surface to attract positively charged molecule of a cationic dye (methylene blue). The initial concentration and pH were a crucial parameter in controlling adsorption process. MB removal percentage by S and NS was decreased at initial concentration increased and pH decreased due to concentration gradient, high mass transfer force and surface charged of sludge-adsorbents.

Adsorption data were analyzed based on the adsorption isotherm and kinetic model. The results showed that MB adsorption onto S and NS could be well described by Langmuir isotherm and the pseudo-second-order kinetic model (correlation coefficient > 0.999). The maximum capacity of S and NS was 82.64 and 90.91 mg/g, respectively. Methylene blue adsorption was a monolayer adsorption and chemisorption process which involved valence force through sharing or the exchange of electron between adsorbent surface (sludge) and adsorbate (MB) as covalent forces. All the systems showed favorable adsorption of the MB with $0< R_L<1$. In addition, the intra-particle diffusion was involved in the adsorption process. The results showed three stage in adsorption process; macro pore diffusion, micro pore diffusion and surface film diffusion.

Adsorption process was also carried out with Fenton-like process to improve the efficiency in methylene blue removal. The comparative study of adsorption and Fenton-like process showed that adsorption with Fenton-like process exhibited higher efficiency than using only adsorption process because of the formation of hydroxyl and perhydroxyl radicals during oxidation, which were the most powerful oxidizaing species. Removal percentage of S and NS in adsorption process was 41.02 and 42.82, respectively. However, adsorption combined with Fenton-like process of S and NS was higher removal percentage with 48.89 and 99.96, respectively. After adding NS, it caused decreasing of pH. This made the favorable condition for oxidation via Fenton-like reaction. Hence, using NS as adsorbent and catalyst for Fenton-like process is higher removal efficiency than S.

Textile wastewater treatment was treated by adsorption with and without Fenton-like process. COD values after treatment of all experiments agreed with industrial effluent standards. Using NS with Fenton-like process showed highest COD removal percentage (72.35%) in 12 h. Adding Fenton-like process into treatment process of S and NS increased the cost operation from 48 to 83 baht and 138 to 173 baht, respectively. However, it offered higher removal efficiency than using only adsorption process. Lastly, water treatment sludge was a highly promising material for the adsorbent production and its conversion represented an alternative choice to existing sludge disposal in a landfill.

Recommendations

1. Modification with chemical method such as potassium hydroxide is interesting to further study in using water treatment sludge as an adsorbent for dye removal.

2. Optimum conditions for dye adsorption should be further studied about the effects of temperature, adsorbent dose and dye type to make a favorable condition for dye adsorption.

3. Reuse and circulation of sludge should be concerned to consider for possible approach in waste management.

4. The economic viability of producing an adsorbent from water treatment sludge on an industrial scale needs to be estimated and assessed.

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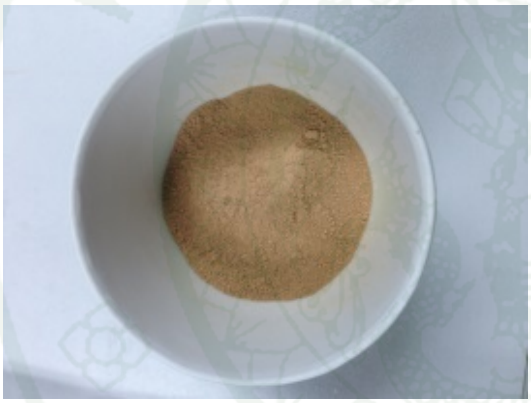
APPENDICES

Appendix A

Sludge-adsorbents

(a)

(b)



(c)

(d)

Appendix Figure A1 Sludge-adsorbent in this study;

(a) Unmodified water treatment sludge, S

(b) Nitric acid modified sludge, NS

(c) Carbonized modified sludge, CS

(d) Carbonized and nitric acid modified sludge, CNS

Appendix B

Adsorption results

Appendix Table B1 Effect of initial concentration in adsorption onto unmodified water treatment sludge (S)

Time	Removal percentage (%)				
(min)	100 mg/L	300 mg/L	500 mg/L	700 mg/L	1,000 mg/L
0	0.00	0.00	0.00	0.00	0.00
1	62.72	26.28	0.87	8.08	7.37
10	95.03	54.04	33.90	30.41	20.28
20	98.07	61.86	39.55	33.68	25.49
30	99.06	68.33	43.13	39.14	28.83
40	99.36	72.03	45.38	42.54	29.65
50	99.46	74.87	46.02	42.51	30.46
60	99.57	76.99	47.19	45.38	31.01
120	99.86	84.21	53.86	50.43	35.56
180		89.34	58.95	50.96	37.04
240		91.75	62.23	51.90	37.80
300		93.68	63.50	52.41	38.25
360		95.02	66.94	53.40	38.85
420		96.05	67.49	54.53	39.50
480		96.16	69.51	54.70	39.68
540		96.37	69.82	54.84	40.35
600		96.49	71.76	55.34	40.65
660			72.19	55.70	40.95
720			72.68	55.72	41.02
780				55.84	41.06

Appendix Table B2 Effect of initial concentration in adsorption onto nitric acid modified water treatment sludge (NS)

Time	Removal percentage (%)				
(min)	100 mg/L	300 mg/L	500 mg/L	700 mg/L	1,000 mg/L
0	0.00	0.00	0.00	0.00	0.00
1	69.91	25.51	16.01	12.96	17.49
10	98.83	67.29	38.15	32.56	26.81
20	99.66	78.07	44.48	39.21	29.63
30	99.82	81.61	46.37	40.93	33.77
40	99.90	84.77	49.86	41.49	34.56
50	99.91	86.53	50.32	42.40	35.21
60	99.95	87.98	52.08	42.54	35.49
120	100.00	93.37	57.63	50.80	38.23
180		95.27	61.29	53.24	38.71
240		96.18	62.22	55.45	40.65
300		97.81	65.21	56.31	41.21
360		98.30	66.46	57.20	41.31
420		98.54	66.39	58.02	41.77
480		98.72	67.14	58.86	42.57
540		98.85	67.20	58.93	42.58
600		98.92	68.09	59.35	42.66
660			68.40	59.43	42.72
720			68.93	59.53	42.82
780				59.63	42.94

Appendix Table B3 Effect of initial pH in adsorption onto unmodified (S) and nitric modified water treatment sludge (NS)

Time	Unmodified water treatment sludge (S)				Nitric acid modified water treatment sludge (NS)			
(min)	pH 2	unbuffer	pH 7	pH 11	pH 2	unbuffer	pH 7	pH 11
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	10.16	7.37	14.19	22.34	12.89	17.49	12.46	37.60
10	18.77	20.28	26.11	37.90	30.05	26.81	24.44	40.73
20	21.08	25.49	30.02	43.67	33.30	29.63	28.24	42.20
30	22.22	28.83	32.87	45.06	35.35	33.77	29.02	46.23
40	25.87	29.65	34.44	47.78	37.70	34.56	32.18	48.13
50	26.92	30.46	36.43	47.95	37.90	35.21	33.11	49.66
60	27.25	31.01	37.10	48.07	38.82	35.49	34.84	52.53
120	31.99	35.56	39.01	49.75	39.95	38.23	36.98	54.64
180	32.77	37.04	39.30	50.69	40.25	38.71	39.12	55.22
240	33.41	37.80	39.33	52.18	40.63	40.65	40.36	56.57
300	34.63	38.25	39.63	52.22	40.92	41.21	40.51	56.78
360	36.10	38.85	40.00	52.45	40.98	41.31	42.32	56.93
420	36.51	39.50	40.04	52.76	41.09	41.77	43.17	56.93

Appendix Table B3 (Continued)

Time	Unmodified water treatment sludge (S)				Nitric acid modified water treatment sludge (NS)			
(min)	pH 2	unbuffer	pH 7	pH 11	pH 2	unbuffer	pH 7	pH 11
480	36.77	39.68	40.25	52.88	41.28	42.57	43.66	57.40
540	36.80	40.35	40.35	53.77	41.34	42.58	43.79	57.47
600	36.86	40.65	40.55	53.80	41.47	42.66	43.86	57.50
660	36.89	40.95	40.83	53.84	41.57	42.72	43.90	57.53
720	36.96	41.02	40.95	53.84	41.59	42.82	43.94	57.58
780	37.00	41.06	40.99	53.89	41.74	42.94	43.97	57.71

Appendix Table B4 Kinetic results of MB adsorption onto unmodified water treatment sludge (S)

Parameter	$q_{e,exp}$(mg/g)	Pseudo-first-order model			Pseudo-second-order model			$t^{1/2}$ (min)
		$q_{e,cal}$(mg/g)	k_1 (h^{-1})	R^2	$q_{e,cal}$(mg/g)	k_2 (g/mg.h)	R^2	
Initial concentration (mg/L)								
100	23.92	17.04	16.38	0.946	24.04	5.77	1.000	0.4
300	60.64	27.55	0.60	0.942	62.11	0.06	0.999	15.7
500	77.82	31.85	0.19	0.838	74.07	0.05	0.999	17.3
700	79.75	33.36	0.40	0.907	80.65	0.05	1.000	14.5
1000	82.79	36.89	0.37	0.914	84.03	0.04	0.999	17.1
Initial pH								
2	79.04	43.32	0.51	0.948	80.65	0.04	0.999	18.9
7	87.16	22.58	0.37	0.781	86.96	0.09	1.000	7.3
11	115.2	28.90	0.39	0.784	116.28	0.07	1.000	7.0

Appendix Table B5 Kinetic results of MB adsorption onto unmodified water treatment sludge (NS)

Parameter	$q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model			$t^{1/2}$ (min)
		$q_{e,cal}$(mg/g)	k_1 (h^{-1})	R^2	$q_{e,cal}$(mg/g)	k_2 (g/mg.h)	R^2	
Initial concentration (mg/L)								
100	23.96	16.48	24.614	0.970	23.98	5.796	1.000	0.4
300	62.21	20.14	0.758	0.809	62.89	0.060	0.999	15.8
500	82.26	44.90	0.200	0.922	80.00	0.040	0.999	18.7
700	86.46	42.48	0.449	0.931	88.50	0.043	1.000	15.9
1000	91.05	32.96	0.415	0.859	91.74	0.035	0.999	18.7
Initial pH								
2	88.64	21.08	0.480	0.747	88.50	2.897	0.999	20.7
7	95.77	45.59	0.675	0.916	98.04	7.286	1.000	8.2
11	122.7	34.22	0.532	0.861	123.46	8.100	1.000	7.4

Appendix Table B6 Intra-particle diffusion parameter of S and NS

pH	$k_{id,1}$	C_1	R_1^2	$k_{id,2}$	C_2	R_2^2
Unmodified sludge (S)						
2	5.3456	19.555	0.9608	0.2614	61.096	0.8922
7	7.0172	28.8040	0.9472	0.5338	79.906	0.9815
11	7.8886	49.68	0.8743	0.7333	101.74	0.9206
Nitric acid modified sludge (NS)						
2	4.6977	30.412	0.8599	0.218	82.757	0.9681
7	6.7725	26.3400	0.9369	0.3731	72.366	0.9101
11	7.5772	72.65	0.9609	0.9564	113.29	0.8502

Appendix Table B7 Langmuir isotherm data of S and NS

Langmuir Isotherm	S		NS	
	C_e	C_e/q_e	C_e	C_e/q_e
100	0.17	0.01	0.00	0.00
300	11.42	0.19	3.61	0.06
500	141.85	1.82	119.64	1.45
700	316.91	3.97	293.94	3.40
1000	594.22	7.18	605.01	6.64

Appendix Table B8 Freundlich isotherm data of S and NS

Freundlich Isotherm	S		NS	
	log C_e	log q_e	log C_e	log q_e
100	-0.77	1.38	-4.50	1.38
300	1.06	1.78	0.56	1.79
500	2.15	1.89	2.08	1.92
700	2.50	1.90	2.47	1.94
1000	2.77	1.92	2.78	1.96

Appendix C

Material cost calculation

Material cost analysis in this study was calculated from electricity bill, tab water supply and chemical cost. Adsorbent material is prepared by different methods including impregnation with nitric acid and carbonization. These costs are calculated to compare each sludge-adsorbent for suitable material selecting in wastewater treatment.

1. Electricity charge

Electricity charge was calculated follow Type 1.1 Metropolitan Electricity Authority (MEA). This consists of 1.1 kW oven using for 12 h. Calculation was expressed by following section.

Section1 Base Tariff

Used energy = Electricity power (kW) x Time (h)
= 1.1 kW x 12 h
= 13.2 units

Energy charge = Electricity energy (unit) x Electricity rate (baht/unit)
= 13.2 x 1.8632
= 32.78 baht

Section 2 Fuel adjustment tariff (F_t) charge

= Used energy x F_t rate
= 13.2 x 0.8544
= 11.28 baht

Section 3 Tax 7%

= (Base Tariff + Ft) x 0.07
= (32.78 + 11.28) x 0.07
= 3.08 baht

Total Electricity Charge = 32.78 + 11.28 + 3.08
= 47.14 baht

2. Nitric acid preparation

Nitric acid was used as chemical agent for sludge modification. This study prepared 1 M nitric acid. Usually, the ratio of sludge to nitric acid is 1 g / 40 ml. The amount of nitric acid solution was normalized with 1 kg dried sludge. Therefore, it was calculated from 40,000 ml by taking 1.8 L of stock solution (25 L) to prepare 1 M nitric acid solution. The cost of 1.8 L equal to 40.32 baht/kg dried sludge. This is shown in calculation. Transportation of sludge is 0.12 baht/kg dried sludge

The amount of nitric acid = Molecular weight (g/ml) x volume (ml)
= 63 g/ml x 40,000 ml
= 2,520 g
= 2,520 g / density
= 2,520 g / 1.4 gml^{-1}
= 1,800 ml (1,8 L)

To prepare 1 M nitric acid, a tap water was used about 38.2 L to mix with 1.8 L nitric acid of stock solution. Price of stock solution is 560 baht, thus this study used only 1.8 L equal to 40.32 baht. Tap water price was based on by Provincial Waterworks Authority (PWA). Minimum of water tariff rate equals to 50 baht.

3. Hydrogen peroxide (H_2O_2)

Hydrogen peroxide was used as chemical agent to form Fenton reagent. It was used only 2 ml 38% H_2O_2 / 1 g dried sludge for all Fenton-like experiment. To normalize the amount of hydrogen peroxide for 1 kg dried sludge, the calculation is shown below.

The amount of 38% H_2O_2 = 2 ml / 1 g dried sludge
The amount of commercial grade 50% H_2O_2 = 1.52 ml / 1 g dried sludge
Price = 1.52 ml/kg x 23 baht/L x 1,000
= 35 baht/ kg dried sludge

Therefore, adsorbent with and without Fenton-like process has different material cost. These costs were shown below.

Adsorption by unmodified sludge (S)

= Transportation + Electricity charge

= 0.12 + 47.14

= 47.26 baht/kg (~48 baht/kg)

Adsorption by nitric acid modified sludge (NS)

= Transportation + Electricity charge + Nitric acid

= 0.12 + 47.14 + (50+40.32)

= 137.58 baht/kg (~138 baht/kg)

Adsorption with Fenton-like process by unmodified sludge (S+Fenton)

= Adsorbent + Hydrogen peroxide

= 48 + 35

= 83 baht/kg

Adsorption with Fenton-like process by nitric acid modified sludge (NS+Fenton)

= Adsorbent + Hydrogen peroxide

= 138 + 35

= 173 baht/kg

Appendix D

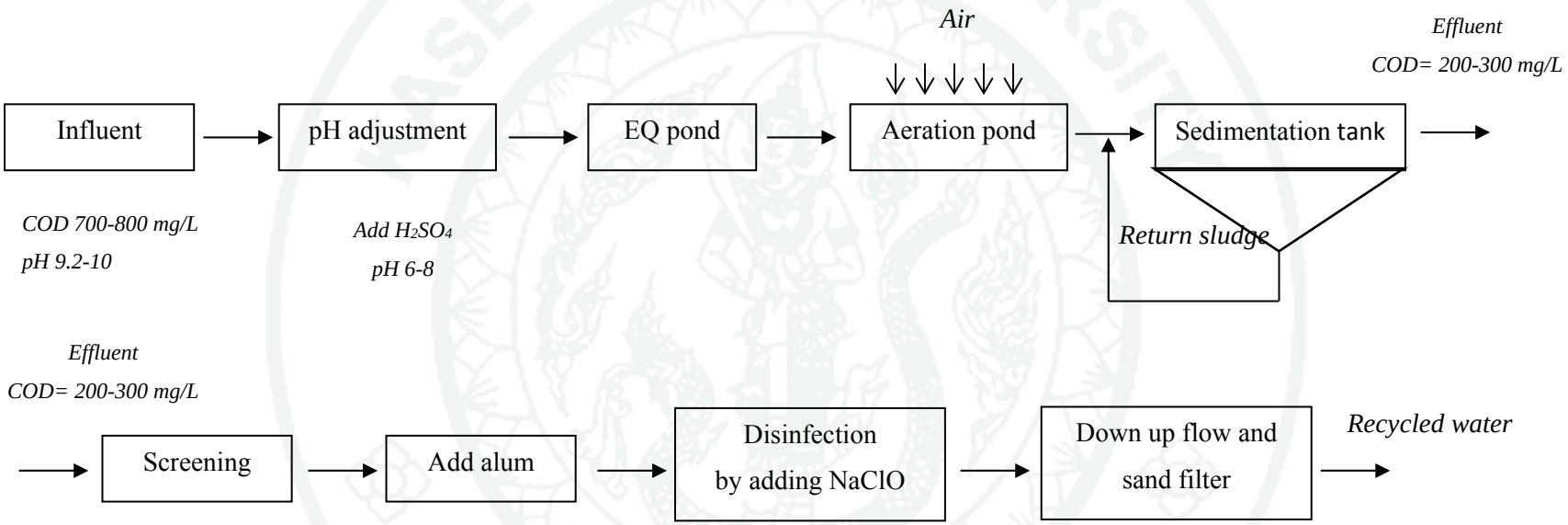
K.World Textile industry

Appendix Figure D1 pH adjustment unit by adding H_2SO_4

Appendix Figure D2 Equalization pond

Appendix Figure D3 Aeration pond

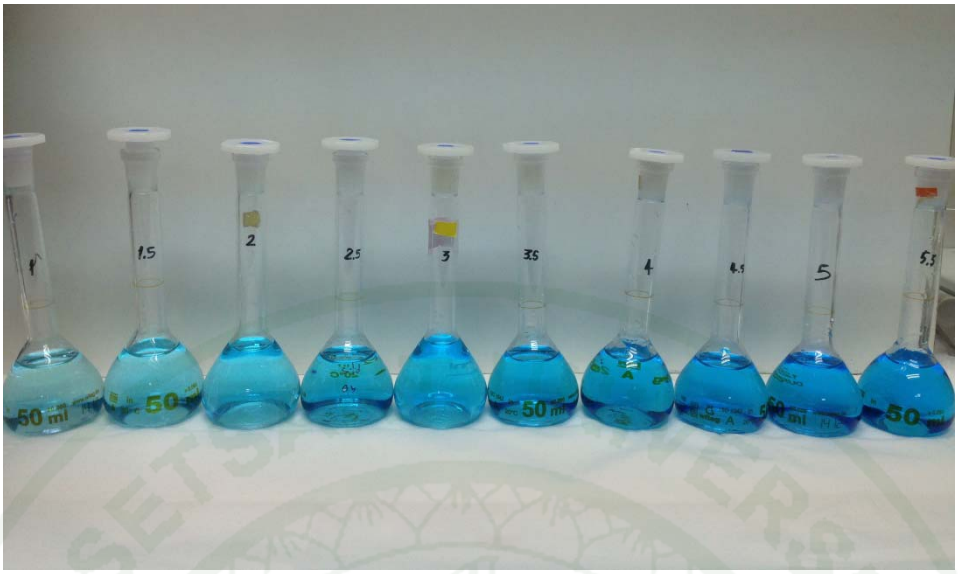
Appendix Fogure D4 Recycling process



Appendix Figure D5 Schematic diagrams of wastewater treatment and recycling process of K.World Textile

Appendix E

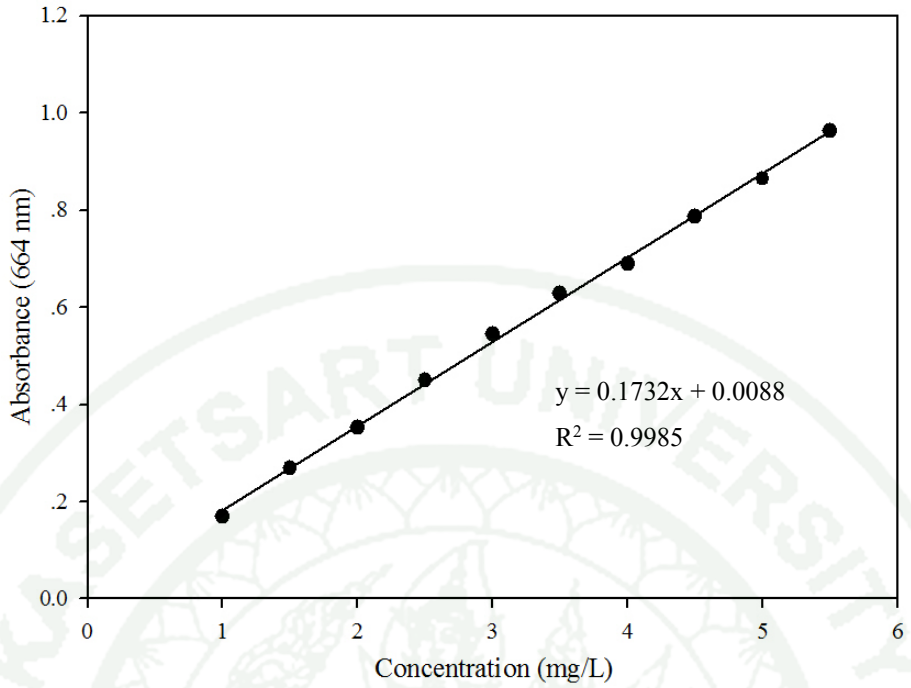
Calibration curve



Appendix Figure E1 Appearance of MB standard solution at different concentrations

Appendix Table E1 MB standard solution and absorbance from UV-vis spectrophotometer

MB concentration (mg/L)	Absorbance (at 664 nm)
1.0	0.16904
1.5	0.26845
2.0	0.35278
2.5	0.44966
3.0	0.54540
3.5	0.62770
4.0	0.68929
4.5	0.78742
5.0	0.86474
5.5	0.96248



Appendix Figure E2 Calibration curve of MB solution

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