REMOVAL OF DYES BY SILICA NANOPARTICLES WITH IMMOBILIZED LACCASE

NURUL SAKINAH BINTI OTHMAN

UNIVERSITI TEKNOLOGI MALAYSIA

REMOVAL OF DYES BY SILICA NANOPARTICLES WITH IMMOBILIZED LACCASE

NURUL SAKINAH BINTI OTHMAN

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To my beloved parent and family

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ABSTRACT

Dyes give a big impact on ecosystem; thus several methods have been developed for dye removal processes. This study investigated the dye removal by the combination of adsorption and biodegradation process. Silica nanoparticles (SN), modified silica nanoparticle (MSN), silica nanoparticle with laccase (SNL), and modified silica nanoparticle with laccase (MSNL) were synthesized. All samples were characterized with scanning electron microscope (SEM), nitrogen adsorption-desorption (NAD), Fourier transform infrared (FTIR), and energy dispersive X-ray (EDX). It was found that the introduction of cationic surfactant and laccase did not change the morphology but it affected the surface area, pore characteristics and chemical properties of the SN. The dye adsorption performance using SN and MSN was evaluated in batch adsorption experiment at various experimental conditions. The adsorption of methylene blue (MB) by SN showed a good adsorption performance (q_e = 0.2291 mmol/g) as compared to the MSN (q_e = 0.0430 mmol/g). In contrast, for methyl orange (MO), the MSN showed a very good adsorption performance (q_e = 0.1849 mmol/g), while no adsorption was observed for the SN. The pH values did not give any significant effect on the dye adsorption and the cetyltrimethylammonium bromide (CTAB) concentration of 1mM was found to be the maximum value for SN modification. The adsorption equilibrium and kinetic data for both MO and MB fit the Temkin and Langmuir isotherm models well, respectively while the kinetic adsorption data follows the Elovich kinetic model with film diffusion found to be the rate-limiting step. The dye adsorption process was found to be exothermic, spontaneous and physisorption. The regeneration shows that SN and MSN are reusable for multiple cycles. For the laccase immobilization, MSN performed higher laccase adsorption (1.6696 μmol/g) as compared to SN (1.1047 μmol/g). The removal of dye by SNL and MSNL was analyzed in term of adsorption and degradation of both MO and MB dyes. Results show that the removal of MB by SNL was higher (q_e = 0.2573 mmol/g) than SN (q_e = 0.2291 mmol/g). Meanwhile, removal of MO by MSNL was higher (q_e = 0.2454 mmol/g) as compared to MSN (q_e = 0.1849 mmol/g). These results demonstrated that the surface modification of SN by cationic surfactant gave higher catalytic activity of laccase, hence giving higher removal performance of dye. The adsorption isotherm data analysis shows that the SNL and MSNL are well fitted to the Langmuir and Temkin model respectively. The Elovich kinetic model is however the best model to describe the dye adsorption kinetic data of both SNL and MSNL. The dye removal by degradation was analyzed using Michaelis-Menten enzymatic reaction equation which found that higher specific activity was observed for MSNL (88.5724 U/g) as compared to SNL (22.6360 U/g). This resulted in higher initial enzymatic reaction velocity, V_{max} (58.0 μM/min) for MO (MSNL) and lower for MB (SNL) (58.0 μM/min).

ABSTRAK

Pencelup memberi kesan buruk kepada ekosistem; jadi beberapa cara penyingkiran dikaji. Kajian ini mengkaji penyingkiran pencelup dengan gabungan proses penjerapan dan penguraian. Silika berzarah nano (SN), silika berzarah nano terubahsuai (MSN), silika berzarah nano dengan lakase (SNL), dan silika berzarah nano terubahsuai dengan lakase (MSNL) telah disintesis. Semua sampel dicirikan dengan mikroskop elektron imbasan (SEM), penganalisis penjerapan-penyahjerapan nitrogen (NAD), spektrometer Fourier transformasi infrared (FTIR) dan pembelau serakan tenaga sinar-X (EDX). Didapati kation surfaktan tidak mengubah morfologi tetapi menjejaskan luas permukaan, ciri liang dan sifat kimia SN. Penjerapan pencelup menggunakan SN dan MSN dinilai dalam eksperimen berkumpulan pada beberapa keadaan. Penjerapan pencelup biru (MB) oleh SN menunjukkan penjerapan yang baik (q_e = 0.2291 mmol/g) berbanding dengan MSN. Sebaliknya, untuk pencelup jingga (MO), MSN menunjukkan penjerapan yang sangat baik (q_e = 0.1849 mmol/g), manakala tiada penjerapan pada SN. Nilai pH tidak memberi kesan yang ketara terhadap penjerapan dan kepekatan *cetyltrimethylammonium bromide* (CTAB) 1 mM didapati adalah nilai maksimum bagi pengubahsuaian SN. Data penjerapan keseimbangan untuk kedua-dua pencelup MO dan MB berkation masing-masing mematuhi model sesuhu *Temkin* dan *Langmuir*, manakala data penjerapan kinetik mematuhi model kinetik *Elovich* dengan resapan filem sebagai kadar yang mengehadkan. Proses penjerapan adalah tindak balas luah haba, spontan dan jerapan fizikal. Penjanaan semula SN dan MSN adalah berjaya untuk beberapa kitaran. Untuk pengubahsuian lakase, MSN menunjukkan penjerapan lakase yang tinggi (1,6696 μmol/g) berbanding SN (1,1047 μmol/g). Penyingkiran pencelup oleh SNL dan MSNL telah dianalisis dari segi penjerapan dan penguraian untuk kedua-dua pencelup MO dan MB. Keputusan menunjukkan bahawa penyingkiran MB oleh SNL adalah tinggi (q_e = 0.2573 mmol/g) daripada SN (q_e = 0.2291 mmol/g). Manakala, penyingkiran MO oleh MSNL adalah tinggi (q_e = 0.2454 mmol/g) berbanding MSN (q_e = 0.1849 mmol/g). Ini menunjukkan pengubahsuaian permukaan SN oleh bahan permukaan berkation meningkatkan aktiviti pemangkinan lakase dan seterusnya memberikan penyingkiran pencelup yang tinggi. Data penjerapan, garis sesuhu menunjukkan bahawa SNL dan MSNL masing-masing mematuhi dengan baik model sesuhu *Langmuir* dan *Temkin*. Model kinetik *Elovich* adalah model yang sesuai bagi penjerapan pencelup oleh SNL dan MSNL. Penyingkiran pencelup secara penguraian pula dinilai menggunakan persamaan tindakbalas enzim *Michaelis-Menten* yang mendapati bahawa aktiviti pemangkin adalah lebih tinggi pada MSNL (88.5724 U/g) jika dibandingkan dengan SNL (22.6360 U/g). Ini membawa kepada kelajuan tindak balas awal enzim, Vmax (58.0 μM / min) yang tinggi untuk MO (MSNL) dan rendah untuk MB (SNL) (58.0 μM/min).

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LIST OF SYMBOLS

b_T	-	Temkin isotherm constant
C_A	-	Final concentration of solute A (mmol/L)
C_{Ao}	-	Initial concentration of solute A (mmol/L)
C_e	-	Equilibrium concentration of the liquid phase (mM)
D_e	-	Effective liquid film diffusion coefficient (cm/min)
D_f	-	Film diffusion coefficient (m^2min^{-1})
d_p	-	Diameter of the particles (nm)
F	-	Ratio of the amount dye adsorbed at time t to the amount at
k_1	-	Rate constant of the pseudo-first order kinetic model (min^{-1})
k_2	-	Rate constant of pseudo-second order kinetic model (mmol/g.min)
K_a	-	The sorption equilibrium constant
K_{DW}	-	Rate constant of adsorption (min^{-1})
K_F	-	Freundlich constant related to the adsorption capacity of the adsorbent
k_{fm1}	-	Equilibrium rate constant of modified pseudo-first order-1
k_{fm2}	-	Equilibrium rate constant of modified pseudo-first order -2
k_{fo}	-	First order chemical rate constant
k_{id}	-	Intraparticle diffusion constant (mmol/g)
K_L	-	Langmuir constant related to monolayer adsorption free energy
k_{sm1}	-	Equilibrium rate constant of modified pseudo-second order-1
k_{sm2}	-	Equilibrium rate constant of modified pseudo-second order-2
k_{so}	-	Equilibrium rate constant of second order adsorption (g/mg.min)
K_T	-	Equilibrium binding constant (L/g)
n	-	Intensity of adsorption
$Ø_{pore}$	-	Pore diameter (nm)
q(r)	-	Local value of solid phase concentration

q_e	-	Adsorption capacity (mmol/g)
Q_{if}	-	Average concentration in the solid at infinite time
q_{max}	-	Maximum adsorption capacity (mg/mol)
Q_s	-	Average value of q (adsorption quantity) in a spherical
q_t	-	Adsorption capacity at time t (min) (mmol/g)
r	-	Radial position
R	-	Universal gas constant (8.314 J/mol.K)
R’	-	Adsorbent particle radius (m)
R^1	-	Liquid film diffusion constant (min^{-1})
r^2	-	Linear regression coefficient for isotherm and kinetic models
R_L	-	Favorabability of dye adsorption on FSN and MSN
r_o	-	Radius of the adsorbent beads
R_p	-	Total particle radius
T	-	Absolute temperature (298 K)
U	-	Laccase activity (μmol/L.min)
V_{pore}	-	Pore volume (cm^3g^{-1})
α	-	Initial adsorption rate (mg/g.min)
β	-	Desorption constant (mg/g.min)
Γ	-	Surface coverage of surfactant (mmol/g)
ΔA	-	Increase in absorbance at 436 nm for laccase
ΔG^o	-	Gibb free energy change (kJ/mol)
ΔH°	-	Enthalpy change (kJ/mol)
ΔS°	-	Entropy change (kJ/mol.K)
χ^2	-	Linear regression coefficient for isotherm and kinetic models
ε	-	Absorptivity of ABTS (29,300 $M^{-1}.cm^{-1}$)

LIST OF ABBREVATIONS

ABTS	-	Azino-bis(3-ethylbenzoline-6-sulfonic acid) diammonium salt
AC	-	Activated carbon
AOP	-	Advanced Oxidation Processes
APD	-	Ambient Pressure Drying
ATR	-	Attenuated Total Reflectance
BET	-	Brunauer-Emmet-Teller
BJH	-	Barrett-Joyner-Halenda
BMCO	-	Blue multicopper oxidases
CI	-	Colour Index
CMC	-	Critical micelle concentration
COD	-	Chemical oxygen demand
CTAB	-	Cethyltrimethylammonium bromide
EDX	-	Energy Dispersive X-Ray
EPR	-	Electron paramagnetic resonance
ETP	-	Effluent treatment plant
FTIR	-	Fourier Transform Infra-Red
HCl	-	Hydrochloric acid
HPLC	-	High performance liquid chromatography
LMS	-	Laccases Mediator Systems
MB	-	Methylene blue
MO	-	Methyl Orange
MSN	-	Modified silica nanoparticles
MSNL	-	Laccase modified silica nanoparticles
NAD	-	Nitrogen Adsorption/Desorption
PFO	-	Pseudo-first-order

PSO	-	Pseudo-second-order
SDS	-	Sodium dodecyl sulphate
SEM	-	Scanning Electron Microscopy
Si-O	-	Silica aerogel
Si-OH	-	Silanol group
SN	-	Silica nanoparticles
SNL	-	Laccase silica nanoparticles
T1	-	Type-1 copper of blue multicopper oxidases
T2	-	Type-2 copper of blue multicopper oxidases
T3	-	Type-3 copper of blue multicopper oxidases
TEA	-	Triethylamine
TEOS	-	Triethoxysilane

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the last century, dyes play an important part in the economy of many countries in which they have been used in many industries such as textile, foods, plastics, leather and pulp industries. Apart of economic benefits, these industries also contribute to water pollution because during processing, 2 - 50% of dyes that are not fixed onto the textile will be discharged as wastewaters (Robinson *et al*., 2001; Wesenberg *et al*., 2003; Murugesan *et al*., 2007; Pandey *et al*., 2007; Khlifi *et al*., 2010). Dyes can give a big impact on ecosystem as they increase the turbidity of water and disturb the photosynthesis process in aquatic flora as well as to cause vomiting, increased heart rate, diarrhea, shock, cyanosis, jaundice, and tissue necrosis on human beings (Chen *et al*., 2011).

Generally, dyes can be categorized into many classes, for instance, based on charge characteristics they can be classified into cationic, anionic and non-ionic dyes. The cationic dye is a basic dye consisting of chromophores from amino groups such as cyanine, hemicyanine and azine that producing color in dyes (Robinson *et al*., 2001). An example of the cationic dyes is methylene blue (MB) which finds wide applications in coloring paper, temporary hair colorant, dyeing for

cottons, wools, coating for paper stock and silk (Rafatullah *et al*., 2010). The anionic dye however consists of chromophores which are mostly from azo and anthraquinone groups. It can be further classified into acid, direct and reactive dyes. Methyl orange (MO) is an example of the acidic anionic dyes which is commonly used in dyeing of textile, printing, paper, wood, pharmaceutical industries, silk, wool, polyamide, modified acrylic and polypropylene fibers (Amran *et al*., 2011). The non-ionic dye refers to disperse dye, also consists of chromophores which are mostly from azo and anthraquinone groups. The non-ionic dye is not ionized in aqueous medium and more resistant to degradation due to their fused aromatic ring structure (Robinson *et al.*, 2001; Fu and Viraraghavan, 2001). They are usually used in dyeing a polyester fiber.

The applications of dyes in many dyeing processes have generating dye wastewaters which require treatment to remove or recover dyes before charging to the surrounding environment. Several methods have been used in removal of dyes include physical (Amran *et al*., 2011; Errais *et al*., 2011; Gil *et al*., 2011), chemical (Fang *et al*., 2010) and biological (Robinson *et al*., 2001; Fu and Viraraghavan, 2001) methods. These methods offer several advantages and drawbacks over others. The combination of adsorption and biodegradation processes has found to be the best method for water re-use in term of flexibility, initial cost and simplicity of the operation, and environmental friendly (Robinson *et al*., 2001; Amran *et al*., 2011).

One of the attractive solution in biodegradation of dyes is based on laccase technologies since it have a high potential in degrading of dyes of diverse chemical structure especially for synthetic dyes (Abadulla *et al*., 2000). Laccase is an extracellular enzyme having molecular weight of approximately 60-70 kDa and the acidic isoelectric point is of around pH 4. It is a monomeric protein, glycoprotein covalently linked to carbohydrate moieties (10 - 45 %) that contributes to its high stability (Durán and Esposito, 2000). Laccase has variety of applications in biotechnology because of its high activity, selectivity and specificity (Mateo *et al*., 2007). The industrial use of the laccase is however still limited due to their relative instable under operational conditions such as high temperature. The exposure to other denaturants and organic solvents through the direct contact of laccase with

organic solvents affect the catalytically active conformation of the laccase (Markvicheva *et al*., 2005).

Therefore, laccase immobilization technology was established to reduce these limitations by increasing the thermostability of the laccase and also it's resistant to the extreme conditions and chemical reagents. Recently, various immobilization methods of laccase have been reported such as covalent bonding, cross-linking, adsorption and entrapment. Among these methods, adsorption is the simplest since it does not require any pre-activation step of the supports which means that the laccase is attached to the matrices of the supports through the non-covalent interactions either by the hydrogen bonding, van der Walls forces, or hydrophobic interactions via the salt linkage (Costa *et al*., 2005; Brena and Viera, 2006). Consequently, many supports have been proposed for immobilization of laccase (Durán and Esposito, 2000). These include organic supports such as natural polymers or synthetic polymers and inorganic supports such as silica materials (Brena and Viera, 2006).

In recent years, many researches focused on silica based porous materials as absorbents such as silica gel (Vihar, 1996), silica aerogel (Liu *et al*., 2010), nanoporous silica (Anbia and Hariri, 2010; Anbia and Salehi, 2012) and mesoporous silicas (Fu *et al*., 2011; Yokoi *et al*., 2012) for dye removal processes because of their large surface area and high dye removal efficiency (Vihar, 1996; Anbia and Hariri, 2010; Fu *et al*., 2011; Yokoi *et al*., 2012). Nevertheless, the use of silica nanoparticles as an adsorbent for dye removal process has hardly reported by any researchers. However, they were used in the separation processes for the removal of BTEX (Kim *et al*., 2013; Kim *et al*., 2014), removal of oil (Cho *et al*., 2014) and extraction of phenolic compound (Zhao *et al*., 2008).

Silica nanoparticles can be synthesized using sol-gel process which is economical, versatile and simple technique. Many synthesis approaches have been reported and it has been found that the templating technique is the most common method used for producing silica nanoparticles with mesoporous structures (Kim *et*

al., 2013; Kim *et al*., 2014). By using surfactant, colloidal crystal, emulsion, latex spheres and even bacteria as the structural templates, the pore size distribution of the porous solid obtained can be controlled (Li *et al*., 2004). The typical examples of this group of silica nanoparticles are SBA-15, MCM-41 and HMM (Fuertes, 2004; Slowing *et al*.,2006; Guan *et al*.,2000). Another approach of course without the use of templating technique producing silica nanoparticles of silica gel types of materials. These include silica cryogel and silica aerogel which depend on the drying procedures adopted in synthesis process. The hydrolysis of silica precursors such as tetraethyl orthosilicate (TEOS) catalyzed by acid or base catalyst followed by the drying process is the most common sol-gel route in silica nanoparticles synthesis.

The silica nanoparticles have basically negative charge surface as a result of partial substitution of Si^{4+} and the excess negative charge can be compensated by exchangeable cations such as Na^{+}, K^{+}, Ca^{2+} or Mg^{2+}. This negative charge surface is due to the presence of Si-O and Si-OH groups make them good absorbents for cationic dyes (Anbia and Hariri, 2010). However, they are unsuitable for adsorption of anionic dyes because of repulsion of the same ionic charge between the silica surfaces and dyes. The surface modification is therefore necessary so that they can be used for various types of dye. It was reported that the surfactant was used in surface modification of zeolites (Alver and Metin, 2012; Jin *et al*., 2008), bentonite (Ozcan *et al*.,2007) and sepiolite (Ozcan and Ozcan, 2005) for removal of dyes.

1.2 Problem Statement

Adsorption is one of the common methods used for treatment of dyes wastewater because it is a simple and economical process. However, this process only involves the transfer of waste dyes from liquid to solid state. The complete elimination of the dyes cannot be achieved solely by adsorption process. One of the attractive solutions to treat the dye wastewaters is by the combination of adsorption

and biodegradation. It was reported that the immobilized laccase has been used for the biodegradation of dyes (Zille *et al*., 2003). The applications of the free and modified silica nanoparticles as adsorbents as well as the enzymatic support have so far not been reported. In this study, the silica nanoparticles were synthesized, modified and used as adsorbents and enzymatic support for removal of dyes from an aqueous solution. The silica nanoparticles will act as absorbent and catalytic support for laccase. It is expected that the dye will be removed by adsorption onto the silica nanoparticles and then will also undergo the biodegradation by the immobilized laccase. The advantages of the silica nanoparticles, among others are non-toxic and biocompatible (Li *et al*., 2004; Cho *et al*., 2014).

1.3 Objectives and Scope of Research

The objectives of this study are:

a) To synthesize, modify and characterize the silica nanoparticles

Silica nanoparticles (SN) were prepared by hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) followed by drying process at ambient temperature and pressure. The synthesized silica nanoparticles were then modified using cationic surfactant (cetyltrimethylammonium bromide, CTAB). The concentration surfactant was determined using two-phase titration technique. The silica nanoparticles (SN) and surfactant modified silica nanoparticles (MSN) were characterized using nitrogen adsorption/desorption analysis (BET), scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FTIR) and elemental composition using Energy Dispersive X-Ray (EDX)

b) To study the dye removal process by adsorption onto silica nanoparticles

The adsorption process of dyes by the silica nanoparticles (SN) and surfactant modified silica nanoparticles (MSN) was studied using methylene blue (MB) and methyl orange (MO) as cationic and anionic dyes, respectively. Adsorption

parameters such as pH, temperature, dye concentration, and contact time were studied. The adsorption data were analyzed using the existing isotherm and kinetic models. The reusability of the SN and MSN was also studied.

c) To study the dye removal process by laccase silica nanoparticles

In this study, the silica nanoparticle (SN) and surfactant modified silica nanoparticle (MSN) were used as supports for the laccase immobilization. The immobilization process was investigated at various pH, initial CTAB concentrations, and initial laccase concentrations. The catalytic activity of laccase was determined by using 2,2'-azino-bis(3-ethylbenzoline-6-sulfonic acid) diammonium salt (ABTS) as a substrate. The thermal stability of SNL and MSNL were also investigated. The performance of the laccase silica nanoparticles (SNL) and laccase modified silica nanoparticles (MSNL) was evaluated using methylene blue (MB) and methyl orange (MO). The amount of the MB and MO degraded by the SNL and MSNL respectively was determined by subtracting the dye removal by SNL and MSNL with respectively by SN and MSN. The dye removal data were analyzed using Michaelis-Menten kinetic model, adsorption isotherm models and kinetic adsorption models.

1.4 Thesis outline

This thesis consists of five chapters. Chapter 1 presents an introduction to the research which comprises of the research background, problem statement, and research objectives and scopes. The detailed discussions about dyes, dye wastewaters and dye removal technologies are presented in Chapter 2. Chapter 3 presents all the methods used in the present study followed by Chapter 4 in which all results are presented and discussed. Chapter 5 summarizes the research findings with some recommendations for future research.

1.5 Summary

The recovery of dyes from dye wastewaters is not economically attractive for dilute dye wastewaters. Adsorption couple with degradation is an attractive technique for removal and thus eliminating dye from such system. Adsorption provides a mean to concentrate the dilute dye and thus degradation it simultaneously which can be achieved at mild conditions using immobilized enzymes such as laccase immobilized on the adsorbent as a support. This will be the subject of the present study towards developing an alternative technology for the dyeing industries for treating their waste before discharging into surrounding environment safely.

REFERENCES

Abadulla, E., Tzanov, T., Costa, S., Robra, K. H., Cavaco-Paulo, and Gübitz, G. M. (2000). Decolorization and detoxification of textile dyes with a laccase from Trametes hirsuta: *Applied and Environmental Microbiology*, 66(8), 3357–62.

Adak, A., Bandyopadhyay, M., and Pal, A. (2005). Removal of anionic surfactant from wastewater by alumina: a case study. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 254(1-3), 165–171.

Adak, A., Pal, A., and Bandyopadhyay, M. (2006). Removal of phenol from water environment by surfactant-modified alumina through adsolubilization. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 277(1-3), 63–68.

Adinew, B. (2012). Textile effluent treatment and decolorization Technique – A review. *Bulgarian Journal of Science Education*, 21 (3), 434-456.

Ahmed, M. and Junin, R. (2009). Equilibrium adsorption isotherm of anionic, nonionic surfactant and their mixtures to shale and sandstone. *Modern Applied Science*, 3, 158-167.

Ahn, M.-Y., Zimmerman, A. R., Martínez, C. E., Archibald, D. D., Bollag, J.-M., and Dec, J. (2007). Characteristics of Trametes villosa laccase adsorbed on aluminum hydroxide. *Enzyme and Microbial Technology*, 41(1-2), 141–148.

Al-Ghouti, M. a., Khraisheh, M. a. M., Allen, S. J., and Ahmad, M. N. (2003). The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. *Journal of Environmental Management*, 69(3), 229–238.

Al-Ghouti, M., Khraisheh, M. a M., Ahmad, M. N. M., and Allen, S. (2005). Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite a kinetic study. *Journal*

of Colloid and Interface Science, 287(1), 6–13.

Ali, H. (2010). Biodegradation of synthetic dyes—A review. *Water Air and Soil Pollution*, 213(1-4), 251–273.

Alkan, M., Demirbaş, O., Celikçapa, S., and Doğan, M. (2004). Sorption of acid red 57 from aqueous solution onto sepiolite. *Journal of Hazadous Materials*, 116(1-2), 135–45.

Allen, S. J., McKay, G., and Porter, J. F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid and Interface Science*, 280(2), 322–33.

Alothman, Z. (2012). A review: Fundamental aspects of silicate mesoporous materisls. *Materials*, 5(12), 2874-2902.

Alpat, S. K., Ozbayrak, O., Alpat, S., and Akçay, H. (2008). The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite. *Journal of Hazadous Materials*, 151(1), 213–20.

Alver, E., and Metin, A. Ü. (2012). Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies. *Chemical Engineering Journal*, 200-202, 59–67.

Amin, N. K. (2009). Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics. *Journal of Hazadous Materials*, 165(1-3), 52–62.

Amran, M., Salleh, M., Khalid, D., Azlina, W., Abdul, W., and Idris, A. (2011). Cationic and anionic dye adsorption by agricultural solid wastes : A comprehensive review: *Desalination*, 280(1-3), 1–13.

Anbia, M., and Hariri, S. A. (2010). Removal of methylene blue from aqueous solution using nanoporous SBA-3. *Desalination*, 261(1-2), 61–66.

Anbia, M., and Salehi, S. (2012). Removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica SBA-3. *Dyes Pigments*, 94(1), 1–9.

Anjaneyulu, Y., Sreedhara, C. and Samuel, S. R. D. (2005). Decolorization of industrial effluents-available methods and emerging technologies-A review. *Reviews in Environmental Science and Biotechnology*, 4(4), 245-273.

Arica, M. Y., Altintas, B., and Bayramoğlu, G. (2009). Immobilization of laccase onto spacer-arm attached non-porous poly(GMA/EGDMA) beads:

application for textile dye degradation. *Bioresource Technology*, 100(2), 665–9.

Armagan, B., Turan, M. and Mehrnet, S. (2004). Equilibrium studies on the adsorption of reactive azo dye in zeolite. *Desalination*, 170, 33-39.

Arroyo, M. (1999). Thermal stabilization of immobilized lipase B from Candida Antartica on different supports: Effect of water activity on enzymatic activity in organic media, *University Complutense, Madrid, Spain*.

Asfour, H.M., Nassar, M. M., Fadali, A., and Geundi, M.S.E. (1985). Color removal from textile effluents using hardwood sawdust as an adsorbent. *Journal of Chemical Technology and Biotechnology*, 35, 28-35

Asgher, M., and Bhatti, H. N. (2012). Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions. *Ecology Engineering*, 38 (1), 79-85.

Azizian, S., and Fallah, R. N. (2010). A new empirical rate equation for adsorption kinetics at solid/solution interface. *Applied Surface Science*, 256(17), 5153–5156.

Badii, K., Ardejani, F. D., Saberi, M. A., Limaee, N. Y., and Shafaei, S. Z. E. D. (2010). Adsorption of acid blue 25 dye on diatomite in aqueous solutions. *Indian Journal of Chemical Technology*, 17(1), 7-16.

Bae, Y.-S., Moon, J.-H., Ahn, H., and Lee, C.-H. (2004). Effects of adsorbate properties on adsorption mechanism in a carbon molecular sieve. *Korean Journal of Chemical Enggineering*, 21(3), 712–720.

Baldrian, P. (2006). Fungal laccases - occurrence and properties. *Institute of Microbiology ASCR*, *30*(2), 215–42.

Banat, I. M., Nigam, P., Singh, D. and Marchant, R. (1997). Microbial decolorization of textile dye containing effluents – a review. Bioresource Technology, 58, 217-227.

Basha, S., Murthy, Z. V. P. and Jha, B. (2009). Sorption of Hg (II) onto Carica Papaya: Experimental studies and design of batch sorber. *Chemical Engineering Journal*, 147, 226-234.

Bautista, L.F., Morales, G. and Sanz, R. (2010). Immobilization strategies for laccase from Trametesversicolor on mesostructured silica materials and the

application to the degradation of naphthalene: *Bioresource Technology*, 101, 8541 – 8548.

Blanco, R. M., Terreros, P., Fernández-Pérez, M., Otero, C., and Díaz-González, G. (2004). Functionalization of mesoporous silica for lipase immobilization. *Journal of Molecular Catalysis B-enzymatic*, 30(2), 83–93.

Bosley, J. a., and Peilow, A. D. (1997). Immobilization of lipases on porous polypropylene: Reduction in esterification efficiency at low loading. *Journal of American Oil Chemist Society*, 74(2), 107–111.

Boushew, A., Shen, X. and Edyvean, R.G. J. (1997). Removal of coloured organic matter by adsorption onto low-cost waste materials. *Water Resource*, 31(8), 2084-2092.

Brena, B., González-pombo, P., and Batista-viera, F. (2006). Immobilization of Enzymes and Cells. 3rd edition. Springer Science and Business Media: New York.

Chen, L., Ramadan, A., Lü, L., Shao, W., Luo, F., and Chen, J. (2011). Biosorption of Methylene Blue from Aqueous Solution Using Lawny Grass Modified withCitric Acid. *Journal of Chemical Enggineering Data*, 56(8), 3392–3399.

Cho, Y. K., Park, E. J. and Kim, Y. D. (2014). Removal of oil by gelatin using hydrophobic silica nanoparticles. *Journal of Industrial and Engineering Chemistry*, 20, 1231-1235.

Chou, T. P., Zhang, Q., Russo, B., Fryxell, G. E., Cao, G. (2007). Titania Particle Size Effect on the Overall Performance of Dye-Sensitized Solar Cells. *Journal of Physical Chemistry C*. 111, 6296–6302.

Choy, K. K. H., Mckay, G., & Porter, J. F. (1999). Sorption of acid dyes from effluents using activated carbon. *Resource, Conservation and Recyling*. 27, 57–71.

Çorman, M. E., Öztürk, N., Bereli, N., Akgöl, S., and Denizli, A. (2010). Preparation of nanoparticles which contains histidine for immobilization of Trametes versicolor laccase. *Journal of Molecular Catalysis B.Enzymatic*. 63(1-2), 102–107.

Costa, S. A., Azevedo, H. S. and Reis, R. L. (2005). Enzymes immobilization in biodegradable polymers for biomedical application. In: Biodegradable system

in tissue engineering and regenerable medicine. R. L. Ries and J. S. Roman edition. CRC Press, London.

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology*, 97(9), 1061–85.

Crini, G., and Badot, P.-M. (2008). Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, 33(4), 399–447.

Cristóvão, R. O., Tavares, A. P. M., Brígida, A. I., Loureiro, J. M., Boaventura, R. a. R., Macedo, E. a., and Coelho, M. A. Z. (2011). Immobilization of commercial laccase onto green coconut fiber by adsorption and its application for reactive textile dyes degradation. *Journal of Molecular Catalysis B.Enzymatic*, 72(1-2), 6–12.

Cristóvão, R. O., Tavares, A. P. M., Ribeiro, A. S., Loureiro, J. M., Boaventura, R. a R., and Macedo, E. a. (2008). Kinetic modelling and simulation of laccase catalyzed degradation of reactive textile dyes. *Bioresource Technology*, 99(11), 4768–74.

Doğan, M., Alkan, M., Türkyilmaz, A., & Ozdemir, Y. (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Materials*, 109(1-3), 141–8.

Dotto, G. L., & Pinto, L. A. A. (2011). Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan : Stirring rate effect in kinetics and mechanism. *Journal of Hazardous Materials*, 187(1-3), 164–170.

Dubinin, M. M. (1960). The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chemical Review*. 60, 235-241.

Durán, N., & Esposito, E. (2000). Potential applications of oxidative enzymes and phenoloxidase-like compounds in wastewater and soil treatment: a review. *Applied Catalysis B: Environmental*, 28(2), 83–99.

Edet, E., Ntekpe, M., and Omereji, S. (2013). Current trend in enzyme immobilization: A review. *International Journal of Modern Biochemistry*, 2, 31-49.

Errais, E., Duplay, J., Darragi, F., Rabet, I. M., Aubert, A., Huber, F., and Morvan, G. (2011). Efficient anionic dye adsorption on natural untreated clay : Kinetic

study and thermodynamic parameters. *Desalination*, 275(1-3), 74–81.

Fang, R., Cheng, X., and Xu, X. (2010). Bioresource Technology Synthesis of lignin-base cationic flocculant and its application in removing anionic azo-dye from simulated wastewater. *Bioresource Technology*, 101(19), 7323–7329.

Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., and Ismadji, S. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of Hazadous Materials.* 162(2-3), 616–45.

Fernández-Fernández, M., Sanromán, M. Á., and Moldes, D. (2013). Recent developments and applications of immobilized laccase. *Biotechnology Advances*, 31(8), 1808–25.

Fernando Bautista, L., Morales, G., and Sanz, R. (2010). Immobilization strategies for laccase from Trametes versicolor on mesostructured silica materials and the application to the degradation of naphthalene. *Bioresource Technology*, 101(22), 8541–8.

Foo, K. Y., and Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2–10.

Forgacs, E., Cserháti, T., and Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. *Environment International*, 30(7), 953–71.

Freundlich, H. M. F. (1906). Uber die adsorption in Lagusen. Z. Physical Chemical, 57 A, 385-470.

Fritz, W. and Schlunder, E. U. (1974). Simultaneous adsorption equilibria of organic solutes in dilute aqueous solution on activated carbon. *Chemical Engineering Science,* 29, 1279-1282.

Fu, X., Chen, X., Wang, J., and Liu, J. (2011). Fabrication of carboxylic functionalized superparamagnetic mesoporous silica microspheres and their application for removal basic dye pollutants from water. *Microporous and Mesoporous. Materials*, 139(1-3), 8–15.

Fu, Y., and Viraraghavan, T. (2001). Fungal decolorization of dye wastewaters: a review. *Bioresource Technology.*, 79(3), 251–62.

Fuangswasdi, A., Charoensaeng, D. A., Sabatini, Scamehorn, J. F., Acosta, E. J., Osathaphan, K., and Khoadhiar, S. (2006). Mixtures of anionic and cationic surfactants with single and twin head groups: Adsorption and precipitation studies. *Journal of Surfactants and Detergents*, 9, 21-28.

Fuertes, A. B. (2004). Synthesis of ordered nanoporous carbons of tunable mesopore size by templating SBA-15 silica materials. *Microporous and Mesoporous Materials*, 67(2-3), 273–281.

Gao, S., Wang, Y., Wang, T., Luo, G., and Dai, Y. (2009). Immobilization of lipase on methyl-modified silica aerogels by physical adsorption. *Bioresource Technology*., 100(2), 996–9.

Garcia-Reyes, R. B. and Rangel-Mendez, J. R. (2010). Adsorption kinetics of chromium(III) ions on agro-waste materials. Bioresource technology, 101 (21), 8099-8108.

Gascón, V., Díaz, I., Márquez-Álvarez, C., and Blanco, R. M. (2014). Mesoporous silicas with tunable morphology for the immobilization of laccase. *Molecules*, , 19(6), 7057–71.

Gil, A., Assis, F. C. C., Albeniz, S., and Korili, S. A. (2011). Removal of dyes from wastewaters by adsorption on pillared clays. *Chemical Engineering Journal*, 168(3), 1032–1040.

Gin, K. Y. H., Tang, T. Z. and Aziz, M. A. (2002). Derivation and application of a new model for heavy metal biosorption by Algae. *Water Resource*, 36, 1313-1323.

Guan, S., Inagaki, S., & Ohsuna, T. (2000). Cubic Hybrid Organic - Inorganic Mesoporous Crystal with a Decaoctahedral Shape, *Journal of American Chemical Society*, 122(10), 5660–5661.

Gupta, V. K. and Suhas (2009). Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management*, 90(8), 2313–2342.

Gupta, V. K., Gupta, B., Rastogi, A., Agarwal, S., & Nayak, A. (2011). A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye--Acid Blue 113. *Journal of Hazardous Materials*, 186(1), 891–901.

Halsey, G. (1948). Physical adsorption on non-uniform surfaces. *Journal of Chemical Physics*, 16, 931-937.

Hameed, B. H., Din, a T. M., & Ahmad, a L. (2007). Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *Journal of Hazardous Materials*, 141(3), 819–25.

Han, Y.-J., Watson, J. T., Stucky, G. D., and Butler, A. (2002). Catalytic activity of mesoporous silicate-immobilized chloroperoxidase. *Journal of Molecular Catalysis B.Enzymatic*, 17(1), 1–8.

Hathway, B. D. E., & Kolar, G. F. (1971). Mechanisms of Reaction between Ultimate Chemical Carcinogens and Nucleic acid. *Ultimate Chemical Carcinogens*, 241-262.

Ho, Y. S., Ng, J. C. Y., and McKay, G. (2011). Kinetics of Pollutant Sorption By Biosorbents: Review. *Seperation and Purification Reviews* 29(2), 189–232.

Huang, Y. (2013). Synthesis and modification of alumina nanofibres and its applicatoins. *Gueenland University of Technology*; Degree of Master Thesis.

Husain, Q and Husain, M. (2012).Environmental Protection Strategies for Sustainable Development. *University of Colorado.: Business Media.*

Igwe, J. C. and Abia, A. A. (2007). Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co (II), Fe (II) and Cu (II) ions from waste water using modified and unmodified maize cob, *International Journal of Physical Science*, 2(5), 119–127.

Jin, X., Jiang, M., Shan, X., Pei, Z., and Chen, Z. (2008). Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite. *Journal of Colloid and Interface Science*, 328(2), 243–7.

Job, N., Théry, A., Pirard, R., Marien, J., Kocon, L., Rouzaud, J.-N., … Pirard, J.-P. (2005). Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials. *Carbon*, 43(12), 2481–2494.

Kalkan, N. A., Aksoy, S., Aksoy, E. A., & Hasirci, N. (2011). Preparation of Chitosan-Coated Magnetite Nanoparticles and Application for Immobilization of Laccase. *Journal of Applied Polymer Science*, 123, 707-716.

Kant, R. (2012). Textile dyeing industry an environmental hazard, Natural Science, 4(1), 22–26.

Karaca, S., Gürses, a., and Bayrak, R. (2004). Effect of some pre-treatments on the adsorption of methylene blue by Balkaya lignite. *Energy Conversion and Management.*, 45(11-12), 1693–1704.

Khan, A. R., Ataullah, R. and Al-Haddad, A. (1997). Equilibrium adsorption studies of some aromatic pollutions from dilute aqueous solutions on activated

carbon at different temperatures. *Journal of Colloid Interface Science*, 194, 154-165.

Khan, R., Bhawana, P. and Fulekar. M. H. (2012). Review Environment Science Biotechnology. *University of Gujarat.: Business Media.*

Khattri, S. D., & Singh, M. K. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption, *Journal of Hazadous Materials*, 167, 1089–1094.

Khlifi, R., Belbahri, L., Woodward, S., Ellouz, M., Dhouib, A., Sayadi, S., and Mechichi, T. (2010). Decolourization and detoxification of textile industry wastewater by the laccase-mediator system. *Journal of Hazadous Materials.*, 175(1-3), 802–8.

Kim, S.-H., Park, J.-H., Hong, Y., & Lee, C.-Y. (2014). Removal of BTX using granular octyl-functionalized mesoporous silica nanoparticle. *International Biodeterioration and Biodegradation. In press*, 1-6

Kim, S.-H., Park, J.-H., and Lee, C.-Y. (2013). Surface-functionalized mesoporous silica nanoparticles as sorbents for BTEX. *Journal of Porous Materials*, 20(5), 1087–1093.

Kitagawa, S., Kitaura, R., and Noro, S. (2004). Functional porous coordination polymers. *Angewandte Chemie (International Ed. in English)*, 43(18), 2334–75.

Koble, R. A. and Corrigan, T. E. (1952). Adsorption isotherm for pure hydrocarbons. *Indian Engineering Chemical*, 44, 383-387.

Kokol.V., Doliska. A.,Eichlerova. I., Baldrian. P., and Nerud. F. (2007).Decolorization of Textile Dyes by Whole Cultures of IschnodermaResinosum and by Purified Laccase and Mn-peroxidese Enzyme and Microbial Technology. *Enzymes and Microbes Technology*., 40, 1673-1677.

Koumanova, B., & Allen, S. J. (2005). decolourisation of water / wastewater using adsorption (review). *Journal of the University of Chemical Technology and Metallurgy*, 40(3), 175–192.

Krishnakumar, S. and Somasundaran, P. (1997). Adsorption of surfactants and polymers at the solid-liquid interface. *Colloids and Surfaces A: Physicochemical and Engibeering Aspects*, 123-124, 491-513.

Kumar, P. S., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., and Sivanesan, S. (2010). Adsorption of dye from aqueous solution by cashew nut shell : Studies on equilibrium isotherm , kinetics and thermodynamics of interactions. *Desalination*, 261(1-2), 52–60.

Kunamneni, A., Ghazi, I., Camarero, S., Ballesteros, A., Plou, F. J., and Alcalde, M. (2008). Decolorization of synthetic dyes by laccase immobilized on epoxy-activated carriers. *Process Biochemistry*, 43(2), 169–178.

Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. *Journal of Americal Society*, 38, 2221-2295.

Leonowicz, A., Edgehill, R. U., and Bollag, J. M. (1984). The effect of pH on the trasformation of syringic and vanillic acids by the laccase of Rhizoctonia praticola and Tranmetes versocolor. *Archieves of Microbiology*, 137, 89-96.

Li, A., Zhu, L., Xu, L., Zhu, W., and Tian, X. (2008). Comparative study on the determination of assay for laccase of Trametes sp., African *Journal of Biochemistry Research*, 2, 181-183.

Li, Z.-Z., Wen, L.-X., Shao, L., and Chen, J.-F. (2004). Fabrication of porous hollow silica nanoparticles and their applications in drug release control. *Official Journal of the Controlled Release Society*, 98(2), 245–54.

Liebminger, S., Siebenhofer, M., and Guebitz, G. (2009). Oxidation of glycerol by 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) in the presence of laccase. *Bioresource Technology.*, 100(20), 4541–5.

Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Barthes, V., and Krimissa, M. (2007). Sorption isotherm: A review on physical bases, modeling and measurement. *Applied Geochemistry*, 22, 249-275.

Liu, G., Yang, R., and Li, M. (2010). Liquid adsorption of basic dye using silica aerogels with different textural properties. *Journal of Non-Crystalline Solids*, 356(4-5), 250–257.

Liu, H., Sha, W., Cooper, A. T., & Fan, M. (2009). Preparation and characterization of a novel silica aerogel as adsorbent for toxic organic compounds. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 347(1-3), 38–44.

Ma, X., Lee, N.-H., Oh, H.-J., Kim, J.-W., Rhee, C.-K., Park, K.-S., and Kim, S.-J. (2010). Surface modification and characterization of highly dispersed silica nanoparticles by a cationic surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 358(1-3), 172–176.

Madhavi, V., and Lele, S. S. (2009). Laccase: Properties and applications. *Bioresources Technology.*, 4(4), 1694–1717.

Mahmoodi, N. M., Khorramfar, S., & Najafi, F. (2011). Amine-functionalized silica nanoparticle: Preparation, characterization and anionic dye removal ability. *Desalination*, 279(1-3), 61–68.

Majeau, J.-A., Brar, S. K., and Tyagi, R. D. (2010). Laccases for removal of recalcitrant and emerging pollutants. *Bioresource Technology*., 101(7), 2331–50.

Markvicheva, E. a., Lozinsky, V. I., Plieva, F. M., Kochetkov, K. a., Rumsh, L. D., Zubov, V. P., Belokon, Y. N. (2005). Gel-immobilized enzymes as promising biocatalysts: Results from Indo-Russian collaborative studies. *Pure and Applied Chemistry*, 77(1), 227–236.

Mateo, C., Palomo, J. M., Fernandez-Lorente, G., Guisan, J. M., and Fernandez-Lafuente, R. (2007). Improvement of enzyme activity, stability and selectivity via immobilization techniques. *Enzyme and Microbial Technology*, 40(6), 1451–1463.

McMullan, G., Meehan, C., Conneely, a., Kirby, N., Robinson, T., Nigam, P., … Smyth, W. F. (2001). Microbial decolourisation and degradation of textile dyes. *Applied Microbiologyand Biotechnology*, 56(1-2), 81–87.

Mohan, D., Gupta, V. K., Srivastava, S. K., & Chander, S. (2001). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 177, 169–181.

Mohan, D., Singh, K. P., Singh, G., & Kumar, K. (2002). Removal of Dyes from Wastewater Using Flyash, a Low-Cost Adsorbent . *Industrial & Engineering Chemistry Research*, 41(15), 3688–3695.

Mohidem, N. A., and Mat, H. Bin. (2012). The catalytic activity enhancement and biodegradation potential of free laccase and novel sol-gel laccase in non-conventional solvents. *Bioresource Technology*, 114, 472–7.

Morozova, O. V, Shumakovich, G. P., Gorbacheva, M. a, Shleev, S. V, and Yaropolov, a I. (2007a). “Blue” laccases. *Biochemistry*, 72(10), 1136–50.

Murugesan, K., and Kalaichelvan, P. T. (2003). Synthetic dye decolourization by white rot fungi. *Indian Journal of Experimental Biology*, 41(9), 1076–87.

Murugesan, K., Nam, I.-H., Kim, Y.-M., and Chang, Y.-S. (2007). Decolorization of reactive dyes by a thermostable laccase produced by Ganoderma lucidum in solid state culture. *Enzyme and Microbial Technology*, 40(7), 1662–1672.

Nandi, B., Goswami, a, and Purkait, M. (2009). Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies. *Applied Clay Science*, 42(3-4), 583–590.

Nigam, P., Armour, G., Banat, I. M., Singh, D., and Marchant, R. (2000). Physical removal of textile dyes from e , uents and solid-state fermentation of dye-adsorbed agricultural residues, *Bioresource Technology*, 72, 219–226.

Nisha, S., S, A. K., and Gobi, N. (2012). A Review on Methods , Application and Properties of Immobilized Enzyme, *Chemical Science Review and Letters*, 1(3), 148–155.

O'Neill, C., Lopez, a, Esteves, S., Hawkes, F. R., Hawkes, D. L., and Wilcox, S. (2000). Azo-dye degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent. *Applied Microbiology and Biotechnology*, 53(2), 249–54.

Oliveira, P. C. De, Alves, G. M., and Castro, H. F. De. (2000). Immobilisation studies and catalytic properties of microbial lipase onto styrene - divinylbenzene copolymer, *Biochemical Engineering Journal*, 5, 63-71.

Osma, J. F., Toca-Herrera, J. L., and Rodríguez-Couto, S. (2010). Biodegradation of a simulated textile effluent by immobilised-coated laccase in laboratory-scale reactors. *Applied Catalysis A: General*, 373(1-2), 147–153.

Osma, J. F., Toca-Herrera, J. L., and Rodríguez-Couto, S. (2010b). Transformation pathway of Remazol Brilliant Blue R by immobilised laccase. *Bioresource Technology*, 101(22), 8509–14.

Ozcan, A., and Ozcan, a S. (2005). Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite. *Journal of Hazardous Materials*, 125(1-3), 252–9.

Ozcan, A., Omeroğlu, C., Erdoğan, Y., and Ozcan, a S. (2007). Modification of bentonite with a cationic surfactant: An adsorption study of textile dye Reactive Blue 19. *Journal of Hazardous Materials*, 140(1-2), 173–9.

Ozdemir, O., Armagan, B., Turan, M., and Çelik, M. S. (2004). Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. *Dyes and Pigments*, 62(1), 49–60.

Öztürk, a., and Malkoc, E. (2014). Adsorptive potential of cationic Basic Yellow 2 (BY2) dye onto natural untreated clay (NUC) from aqueous phase: Mass transfer analysis, kinetic and equilibrium profile. *Applied Surface Science*, 299, 105–115.

Pandey, A., Singh, P., and Iyengar, L. (2007). Bacterial decolorization and degradation of azo dyes. *International Biodeterioration and Biodegradation*, 59(2), 73–84.

Paria, S., and Khilar, K. C. (2004). A review on experimental studies of surfactant adsorption at the hydrophilic solid – water interface. *Dalhouse University*.

Patel, R. P., Purohit, N. S., and Suthar, A. M. (2009). An Overview of Silica Aerogels. *International Journal of ChemTech Research*, 1(4), 1052–1057.

Perdigoto, M. L. N., Martins, R. C., Rocha, N., Quina, M. J., Gando-Ferreira, L., Patrício, R., & Durães, L. (2012). Application of hydrophobic silica based aerogels and xerogels for removal of toxic organic compounds from aqueous solutions. *Journal of Colloid and Interface Science*, 380(1), 134–40.

Pereira, L., and Alves, M. (2010). Dyes-Environmental Impact and Remediation. *Springer Science and Business Media.*

Pereira, L., Pereira, R., Pereira, M. F. R., van der Zee, F. P., Cervantes, F. J., and Alves, M. M. (2010). Thermal modification of activated carbon surface chemistry improves its capacity as redox mediator for azo dye reduction. *Journal of Hazardous Materials*, 183(1-3), 931–9.

Pereira, M. F. R., Soares, S. F., and Figueiredo, L. (2003). A dsorption of dyes on activated carbons : influence of surface chemical groups, *Carbon*, 41, 811–821.

Pielesz, a., Baranowska, I., Rybak, a., and Włochowicz, a. (2002). Detection and Determination of Aromatic Amines as Products of Reductive Splitting from Selected Azo Dyes. *Ecotoxicology and Environmental Safety*, 53(1), 42–47.

Pierre, A. C., and Pajonk, G. M. (2002). Chemistry of aerogels and their applications. *Chemical Reviews*, 102(11), 4243–65.

Pierre, A. C. and Rigacci, A. (2011). Silica aerogels. *Advances in Sol-Gel Derived Materials and Technologies*, 21-45.

Piontek, K., Antorini, M., and Choinowski, T. (2002). Crystal structure of a laccase from the fungus Trametes versicolor at 1.90-A resolution containing a full

complement of coppers. *The Journal of Biological Chemistry*, 277(40), 37663–9.

Pouretedal, H. R., and Kazemi, M. (2012). Characterization of modified silica aerogel using sodium silicate precursor and its application as adsorbent of Cu 2 + , Cd 2 + , and Pb 2 + ions. *International Journal of Industrial Chemistry*, 3(1), 1.

Puanngam, M., and Unob, F. (2008). Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions. *Journal of Hazardous Materials*, 154(1-3), 578–87.

Qin, G., Yao, Y., Wei, W., & Zhang, T. (2013). Preparation of hydrophobic granular silica aerogels and adsorption of phenol from water. *Applied Surface Science*, 280, 806–811.

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W., and Zhang, Q. (2009). Critical review in adsorption kinetic models , *Journal of Zhejiang University*, 10(5), 716–724.

Radke, C. J. and Parausnitz, J. M. (1972). Adsorption of organic solutes from dilute aqueous solution of activated carbon. *Indian Engineering Fundamental*, 11, 445-451.

Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents : A review. *Journal of Hazardous Materials*, 177(1-3), 70–80.

Rao, a. P., Rao, a. V., and Pajonk, G. M. (2007). Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents. *Applied Surface Science*, 253(14), 6032–6040.

Rao, M. M., Ramana, D. K., Seshaih, K., Wang, M. C., and Chien, S. W. C. (2009). Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls. *Journal of Hazadous Materials*, 166, 1006-1013.

Redlich, O. and Peterson, D. L. A. (1959). A useful adsorption isotherm. *Journal of Physical Chemistry*, 63, 1024-1026.

Rengaraj, S., Kim, Y., Joo, C. K., and Yi, J. (2004). Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas : kinetics and equilibrium. *Journal of Colloid and Interface Science*, *273*, 14–21.

Rennie, S. (1999). Adsorption of styryl pyridinium dyes on CTAB treated silica. *Langmuir*, 6(5), 639–645.

Robinson, T., McMullan, G., Marchant, R., and Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77(3), 247–55.

Saman, N., Johari, K., and Mat, H. (2014). Adsorption Characteristics of Sulfur-Functionalized Silica Microspheres with Respect to the Removal of Hg(II) from Aqueous Solutions. *Industrial and Engineering Chemistry Research*, 53(3), 1225–1233.

Sarawade, P. B., Kim, J.-K., Hilonga, A., and Kim, H. T. (2010). Influence of aging conditions on textural properties of water-glass-based silica aerogels prepared at ambient pressure. *Korean Journal of Chemical Engineering*, 27(4), 1301–1309.

Shuler, M.L and Kargi, F. (2005). Bioprocess Engineering. (2nd Edition). Upper Saddle River, N.J.: Prentice Hall.

Slejko, F. L. (1985). *Adsorption technology: A step-by-step approach to process evaluation and application*. United stated of America: Marcel Dekker, Inc.

Slowing, I., Trewyn, B. G., & Lin, V. S. (2006). Effect of Surface Functionalization of MCM-41-Type Mesoporous Silica Nanoparticles on the Endocytosis by Human Cancer Cells, *Journal of American Chemical Society*, 128, 14792–14793.

Smith, J. M. (1970). Chemical Engineering Kinetics. (2nd edition) New York: McGraw-Hill Inc.

Soleimani Dorcheh, a., & Abbasi, M. H. (2008). Silica aerogel; synthesis, properties and characterization. *Journal of Materials Processing Technology*, 199(1-3), 10–26.

Srinivasan, A., and Viraraghavan, T. (2010). Decolorization of dye wastewaters by biosorbents : A review. *Journal of Environmental Management*, 91(10), 1915–1929.

Standeker, S., Novak, Z., & Knez, Z. (2009). Removal of BTEX vapours from waste gas streams using silica aerogels of different hydrophobicity. *Journal of Hazardous Materials*, 165(1-3), 1114–8.

Štandeker, S., Veronovski, A., Novak, Z., & Knez, Ž. (2011). Silica aerogels modified with mercapto functional groups used for Cu(II) and Hg(II) removal from aqueous solutions. *Desalination*, 269(1-3), 223–230.

Stolz, a. (2001). Basic and applied aspects in the microbial degradation of azo dyes. *Applied Microbiology and Biotechnology*, 56(1-2), 69–80.

Tadayon, F. and Motahar, S. (2012). Modified silica aerogel nanoparticles: adsorbent for the preconcentration of mercury in human air. Sharif University of Technology, 96 – 98.

Takahashi, H., Li, B., Sasaki, T., Miyazaki, C., Kajino, T., and Inagaki, S. (2001). Immobilized enzymes in ordered mesoporous silica materials and improvement of their stability and catalytic activity in an organic solvent. *Microporous and Mesoporous Materials*, 44-45, 755–762.

Tan, I. A. W., Ahmad, A. L., and Hameed, B. H. (2009). Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *Journal of Hazadous Materials*, 164, 473-482.

Temkin, M. J., and Pyzhew, V. (1940). Recent modifications to Langmuir isotherm. *Acta Physico-Chemica*, 12, 217-222.

Toth, J. (2000). Calculation of the BET-compatible surface area from any type I isotherm measured above the critical temperature. *Journal of Colloid and Interface Science*, 225, 378-383.

Trompette, J. L., Zajac, J., Keh, E., and Partyka, S. (1994). Scanning of the cationic surfactant adsorption on a hydrophilic silica surface at low surface coverages. *Langmuir*, 10, 812-818.

Vadivelan, V., and Kumar, K. V. (2005). Equilibrium , kinetics , mechanism , and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science*, 286, 90–100.

Verma, A. K., Dash, R. R., and Bhunia, P. (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*, 93(1), 154–68.

Vihar, J. (1996). Adsorption of Styryl Pyridinium Dyes on Silica Gel. *Journal of Colloid and Interface Science*, 477, 473–477.

Vimonses, V., Lei, S., Jin, B., Chow, C. W. K., and Saint, C. (2009). Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, *Chemical Engineering Journal*, 148, 354–364.

Vineis, P., and Pirastu, R. (1997). Aromatic amines and cancer. *Cancer Causes and Control* , 8(3), 346–55.

Wang, F., Guo, C., Yang, L., and Liu, C.-Z. (2010). Magnetic mesoporous silica nanoparticles: fabrication and their laccase immobilization performance. *Bioresource Technology*, 101(23), 8931–5.

Wang, J., Peng, C. S., Yang, Z. F., Li, D. D., and Wu, Y. T. (2013). Adsorption and Regeneration Characteristics of Granular Adsorbent Based on Coal Fly Ash for Methylene Blue Removal. *Advanced Materials Research*, 773, 899–906.

Webb, P. A. and Orr, C. (1997). Analytical methods in fine partile technology. Nacross, Ga, USA: Micromeritics Instrument Corporation.

Weber, J. R. (1985). *Adsorption theory, concept and models, adsorption technology: A step-by-step approach to process evaluation and application*. New York and Basel: Marcel Dekker, Inc.

Wesenberg, D. (2003). White-rot fungi and their enzymes for the treatment of industrial dye effluents. *Biotechnology Advances*, 22(1-2), 161–187.

Wu, C. N., Ling, Q., Wang, L., Li, W. H., Tang, Y. C., Tao, Y., … Li, Y. (2012). Removal of Methylene Blue from Wastewater Using Zeolite from Fly Ash. *Advanced Materials Research*, 610-613, 1286–1289.

Xu, X., Lu, P., Zhou, Y., Zhao, Z., & Guo, M. (2009). Laccase immobilized on methylene blue modified mesoporous silica MCM-41/PVA. *Materials Science and Engineering: C*, 29(7), 2160–2164.

Yang, X., and Al-Duri, B. (2005). Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. *Journal of Colloid and Interface Science*, 287(1), 25–34.

Yokoi, T., Kubota, Y., and Tatsumi, T. (2012). Amino-functionalized mesoporous silica as base catalyst and adsorbent. *Applied Catalysis A: General*, 421-422, 14–37.

Zhang, R., and Somasundaran, P. (2006). Advances in adsorption of surfactants and their mixtures at solid / solution interfaces. *Advances in Colloid and Interface Science*, 126, 213–229.

Zhao, X., Shi, Y., Wang, T., Cai, Y., and Jiang, G. (2008). Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples. *Journal of Chromatography. A*, 1188(2), 140–7.

Zhou, Z., and Hartmann, M. (2012). Recent Progress in Biocatalysis with Enzymes Immobilized on Mesoporous Hosts. *Topics in Catalysis*, *55*(16-18), 1081–1100.

Zhu, Y., Kaskel, S., Shi, J., Wage, T., and Pee, K.V. (2007). Immobilization of Trametesversicolorlacaase on magnetically separable mesoporous silica spheres: *Chemical Materials*. 19, 6408 – 6413.

Zille, A., Tzanov, T., Gübitz, G. M., and Cavaco-Paulo, A. (2003). Immobilized laccase for decolourization of Reactive Black 5 dyeing effluent. *Biotechnology Letters*, 25(17), 1473–7.