

# METHYLENE BLUE ADSORPTION ONTO CROSSLINKED SAGO STARCH

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*Special Dedication of This Grateful Feeling to My Beloved father and mother;*

*Mr. MUHMEDB. ALI and Mrs. HABSAH BT. AB. KADIR*

*Loving siblings;*

*NOR NAZIFAH, SALIHAN KAMILAH,*

*MOHD IHSAN ADLI and MOHD SALAHUDDIN*

*For Their Love, Support and Best Wishes.*

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## ABSTRACT

Crosslinked sago starch was prepared by crosslinking native sago starch with sodium trimetaphosphate (CSS-STMP) and epichlorohydrin (CSS-EPCH) as renewable adsorbents. CSS-STMP and CSS-EPCH were used to remove methylene blue (MB) from aqueous solution based on its characterization tests. The adsorption capacity of CSS-STMP and CSS-EPCH were evaluated as a function of pH, adsorbent dosage, initial MB concentration, contact time and temperature. It was favorable for adsorption under condition of pH 7 and at 50 ppm for both adsorbent. The adsorption capacity trend was reduced with increasing adsorbent dosage where 0.05 g dose of adsorbent was chosen. Equilibrium adsorption capacity ( $q_e$ ) of MB adsorption onto CSS-STMP and CSS-EPCH were  $2.224 \text{ mg g}^{-1}$  and  $1.303 \text{ mg g}^{-1}$ , respectively. CSS-STMP adsorbent was employed for further experiment due to its better performance than CSS-EPCH. The equilibrium isotherms were conducted using Langmuir, Freundlich and Tempkin models. It has been demonstrated that a better agreement was Langmuir isotherm with a correlation coefficient ( $R^2$ ) of 0.990, complete monolayer adsorption capacity ( $q_m$ ) of  $3.731 \text{ mg g}^{-1}$ , chi-square test ( $\chi^2$ ) of 0.029% and corresponding contact time of 4 hours. The pseudo-first-order, pseudo-second-order and intra-particle diffusion were used to fit adsorption data in the kinetic studies. The results show that the adsorption kinetic was more accurately described by the pseudo-second-order model with the mechanism via film diffusion where  $R^2$  is 0.999 and variance is 0.152%. The adsorption of MB on CSS-STMP was exothermic and non-spontaneous in nature at temperature of 303K. Regeneration study also indicated that CSS-STMP adsorbent have the potential to be reused at the same adsorption performance for numbers of cycle. The obtained results suggest that CSS-STMP could be a promising candidate as an adsorbent for MB removal.

## ABSTRAK

Kanji sagu ikatan-silang disediakan dengan mengikat silang kanji sagu dengan natrium trimetafosfat (CSS-STMP) dan epiklorohidrin (CSS-EPCH) sebagai penjerap yang boleh diperbaharui. CSS-STMP dan CSS-EPCH digunakan untuk menyingkirkan metilena biru (MB) daripada larutan akueus berdasarkan ujian pencirian. Kapasiti penjerapan oleh CSS-STMP dan CSS-EPCH dinilai berdasarkan pH, dos penjerap, kepekatan awal MB, hubungan masa dan suhu. Proses penjerapan adalah lebih tinggi pada pH 7 dan kepekatan awal MB sebanyak 50 ppm untuk kedua-dua penjerap. Trend kapasiti penjerapan berkurangan apabila dos penjerap bertambah di mana dos penjerap 0.05 g telah dipilih. Kapasiti penjerapan ( $q_e$ ) oleh CSS-STMP dan CSS-EPCH masing-masing adalah sebanyak  $2.224 \text{ mg g}^{-1}$  dan  $1.303 \text{ mg g}^{-1}$ . Penjerap CSS-STMP digunakan untuk uji kaji seterusnya disebabkan prestasi yang lebih baik berbanding CSS-EPCH. Oleh itu, penjerap CSS-STMP digunakan untuk eksperimen seterusnya. Keseimbangan isoterma dijalankan menggunakan model Langmuir, Freundlich dan Tempkin. Isoterma Langmuir menunjukkan prestasi baik dengan nilai korelasi pekali ( $R^2$ ) 0.990, satu lapisan lengkap kapasiti penjerapan ( $q_m$ )  $3.371 \text{ mg g}^{-1}$ , ujian khi kuasa dua ( $\chi^2$ ) 0.029% yang sepadan dengan masa sentuhan 4 jam. Pseudo peringkat-pertama, pseudo peringkat-kedua dan penyebaran intra zarah digunakan untuk menyesuaikan data penjerapan di dalam kajian kinetik. Keputusan menunjukkan penjerapan kinetik adalah lebih tepat diterangkan oleh model pseudo peringkat-kedua dengan mekanisme melalui filem penyebaran di mana nilai korelasi pekali ialah 0.999 dan nilai varians ialah 0.152%. Penjerapan MB oleh CSS-STMP adalah luah haba dan bukan spontan pada suhu 303K. Kajian pertumbuhan semula menunjukkan CSS-STMP mampu untuk digunakan semula pada prestasi penjerapan yang sama. Keputusan yang diperoleh mencadangkan bahawa CSS-STMP boleh dijadikan penjerap alternatif yang baik untuk penyingkiran MB.

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## LIST OF SYMBOLS

$\Delta G^\circ$	-	Gibbs free energy change
$\Delta H^\circ$	-	Enthalpy change of adsorption
$\Delta H_g$	-	Enthalpy of gelatinization
$\Delta S^\circ$	-	Entropy change of adsorption
$b_T$	-	Heat of adsorption ( $\text{J mol}^{-1}$ )
$C_e$	-	Equilibrium concentration ( $\text{mg L}^{-1}$ )
$C_0$	-	Initial Concentration ( $\text{mg L}^{-1}$ )
$H^+$	-	Hydrogen ion
$k_1$	-	Rate constant of pseudo-first order model ( $\text{min}^{-1}$ )
$k_2$	-	Rate constant of pseudo-second order model ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_D$	-	The distribution coefficient ( $\text{L g}^{-1}$ )
$K_F$	-	Equilibrium adsorption constant for Freundlich model ( $\text{L g}^{-1}$ )
$k_i$	-	Rate constant of intra-particle diffusion ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )
$K_L$	-	Equilibrium adsorption constant for Langmuir model ( $\text{L mg}^{-1}$ )
Ma		Moisture content
Mb	-	Bound water content
n	-	Heterogeneity factor in Freundlich isotherm
$O_3$	-	Ozone
$q_e$	-	Equilibrium adsorption capacity ( $\text{mg g}^{-1}$ )
$q_{e,cal}$	-	Calculated equilibrium adsorption capacity ( $\text{mg g}^{-1}$ )
$q_{e,exp}$	-	Experimental equilibrium adsorption capacity ( $\text{mg g}^{-1}$ )
$q_{max}$	-	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )
$q_t$	-	Adsorption capacity at time t ( $\text{mg g}^{-1}$ )

$R$	-	The gas constant (8.314 J/(mol K))
$R \%$	-	Percentage of removal
$R^2$	-	Correlation coefficients
$R_L$	-	Separation factor in Langmuir isotherm
$T$	-	Absolute temperature (K)
$T_c$	-	End temperature
$T_o$	-	Onset temperature
$T_p$	-	Peak temperature of gelatinization
$\alpha_T$	-	Tempkin isotherm constant ( $L g^{-1}$ )
$\lambda$	-	Wavelength
$\chi^2$	-	Chi-square test

**LIST OF ABBREVIATIONS**

BOD	-	Biochemical Oxygen Demand
Ca(OH) <sub>2</sub>	-	Calcium Hydroxide
CSS-EPCH	-	Crosslinked Sago Starch with Epichlorohydrin
CSS-STMP	-	Crosslinked Sago Starch with Sodium Trimetaphosphate
DSC	-	Differential Scanning Calorimeter
EPCH	-	Epichlorohydrin
EtOH	-	Ethanol
FTIR	-	Fourier Transform Infrared
HCl	-	Hydrochloric Acid
KOH	-	Potassium Hydroxide
MB	-	Methylene Blue
Na <sub>2</sub> CO <sub>3</sub>	-	Sodium Carbonate
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
NH <sub>4</sub> OH	-	Ammonium Hydroxide
POCl <sub>3</sub>	-	Phosphorus Oxychloride
SEM	-	Scanning Electron Microscopy
STMP	-	Sodium Trimetaphosphate
STPP	-	Sodium Tripolyphosphate
TGA	-	Thermogravimetric Analysis
TSS	-	Total Suspended Solid
XRD	-	X-ray Diffraction



## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Water contamination resulting from dyes which are partly discharged into the rivers and lakes, altering the biological stability of surrounding ecosystems has aroused concern (Deng *et al.*, 2011). Safe and clean water is important to reduce the chances of getting undesired effects caused by polluted water. Dyes are the main constituent used in a major process for industries such as textile, paint, tannery, paper and pulp, and dyeing in return produced a substantial amount of coloured wastewater. In addition to being aesthetically displeasing, dyes contain in water are also harmful to human health and inhibit the sunlight penetration into the water which directly destruct the aquatic ecosystem. In addition, the coloured effluence also triggers an increasing toxicity and carcinogenic harm (Wang *et al.*, 2014). Therefore, these coloured wastewater effluents must to be treated before discharge.

Currently, there are many methods for the removal of dyes from industrial effluent for example flocculation (Szyguła *et al.*, 2009; Verma *et al.*, 2012), adsorption (Guo *et al.*, 2013), filtration (Zhang *et al.*, 2013; Ellouze *et al.*, 2012), and

biological process. Conventional technologies for waste water treatment such as oxidation, biodegradation and ozonation are not practically used to remove dyes since dyes are a stable constituent with a complex aromatic molecular structure, making it difficult to be removed (Wang *et al.*, 2014). Among these technologies available, adsorption is a promising technique being practised today basically due to its being economical, simplicity of design and operation yet effective. The adsorption mechanism is referred to the gradual transition of the dye from the solution onto the surface of the adsorbent reaches a point after which allocation of the dye between the adsorbent in the solution remains unchanged.

Numerous approaches on different adsorbents such as activated carbon, saw dust, zeolites, chitin, chitosan, silica and others have been examined on the potential of dye concentrations removal from aqueous solutions. In order to enhance the adsorption capability, it becomes a major target to evolve more effective and low-cost adsorbent with a great performance of adsorption capacities. Suitable adsorbents used in dye adsorption process are activated carbon, silica, rice husk, coconut husk, saw dust, chitin, chitosan, starch and so forth. Many adsorbents have been tested for their removal ability but most of them are non-regenerable throwaway products. However, this research will assess the potential of using crosslinked sago starch as adsorbent that can be easily regenerated to absorb dye.

Next to cellulose, starch is found to be the most plentiful carbohydrate that exists from plant kingdom as a natural raw material. Sago starch is derived from *Metroxylonsagu* and grows well in Southeast Asian countries as a tropical crop (Abdorreza *et al.*, 2012). Sago starch is qualified for the material in this research due to comparatively low-cost and abundance in Malaysia particularly in Sarawak. Being a biodegradable polymer along with well-defined chemical properties and structure, sago starch owns a great possibility as a flexible resource for numerous material applications particularly in industrial areas. Further, other characteristics possessed by sago starch include its abundance, biocompatibility, non-toxicity, and

antibacterial property make it an exceptional choice for the raw material (Renault *et al.*, 2008).

Hydrophilic nature in starch becomes a major constraint which can limit its application in engineering field as well as the development of starch-based material. Therefore chemical modification is applied to enhance the structure and properties of starch which become the solution for this problem where a water resistance adsorbent is then developed (Renault *et al.*, 2008). Chemical modification made is expected to accumulate chemical bonds at random sites inside the granule. Hence, resulting in the stabilization of the granules as well as intensifying the relatively tender starch (Singh and Nath, 2012). Crosslinked starch slurry is highly viscous and is less prone to rupture with either extended period of heating, increasing acidic content or even harsh shaking. Cross-linking agents can provide a cross-linked sago starch to be use for various food and non-food applications. In spite of the changes in physical properties of starch by modification made through cross-linking, thermal transition characteristics can be altered as well (Mirmoghtadaie *et al.*, 2009).

The sago bio-sorbent prepared in this research is expected to have a high adsorption capacity and that the desorbed sago adsorbent is recycled to adsorb the dye again and will acquire an identical adsorption capacity performance as that before the recycle. The sorbent is also expected to be technically feasible to remove dyestuffs from an aqueous solution that will reduce water pollution.

## 1.2 Problem Statement

The adsorption technique is a promising method amongst all techniques available in dye removal treatment due to its high efficiency, low-cost, and simplicity in design and operation (Yu *et al.*, 2012). A good selection of solid sorbent becomes one of the biggest problems in adsorption technique. An adsorbent should possess characteristics of adsorbing maximum pollutant economically, biodegradable, high stability, renewable and the sources are abundant in nature. These factors have encouraged many researchers to investigate the alternative efficient and low-cost adsorbents. In this study, starch is selected since it is low-cost and renewable materials (Janaki *et al.*, 2012), abundant in nature, great capability to adsorb and effective adsorbent for handling dyes (Xu *et al.*, 2006). Among all starch derivatives presented, sago starch is chosen as adsorbent to remove dye since it is possess a capability to adsorb, renewable, abundant and cheaper in Malaysia.

In spite of several advantages present, sago starch suffers from its hydrophilic nature which becomes a limiting factor for developing of starch-based material. Chemical modification through crosslinking is introduced to stabilize the tender structure of sago starch. Crosslinking is the most commonly used way to modify starch, intended to add intra- or inter- molecular bond at random location of starch molecule (Gao *et al.*, 2014). In this research, a crosslinked sago starch is believed to have a maximum adsorption capacity with a high potential to be easily regenerated to readsorb dye in order to reduce process cost as well as reduce the environmental problem and becomes a biodegradable dye adsorbent.

### **1.3 Research Objectives**

Chemical modification is made to the sago starch in order to enhance the mechanical strength of adsorbent, which finally forms a crosslinked sago starch. These promising adsorbents will possess a huge potential to remove dyestuff from water through adsorption.

This study embarks on the following objectives:

- i To synthesize and analyse the characterizations of crosslinked sago starch as adsorbent
- ii To investigate the equilibrium isotherms, kinetics and thermodynamic study of adsorption behaviour of crosslinked sago starch in aqueous solution with respect to temperature, solution pH value, adsorbent dosage, initial concentration, contact time and temperature.
- iii To assess the reusability of desorbed crosslinked sago beads to re-adsorb dye efficiently and examine the potential of crosslinked sago starch as an adsorbent.

### **1.4 Scopes of Research**

The following are the scopes in this research to support the above mentioned objectives:

- i) To synthesize and analyse the characterizations of crosslinked sago starch adsorbent.

Sago starch adsorbent is prepared and synthesized through a chemical modification and some other procedures as explained in Chapter 3. The characteristics of the adsorbent is analysed based on surface morphology determination on scanning electron microscope (SEM), structure and chemical composition determination by x-ray diffraction (XRD), functional group determination using Fourier transform infrared (FTIR), differential scanning calorimeter (DSC) used to study the thermal behaviour of starch including gelatinization, and finally thermogravimetric analysis (TGA) is employed to identify the stability of starch and its retrogradation properties are evaluated.

- ii) To investigate the equilibrium isotherms, kinetics and thermodynamic study of adsorption behaviour of crosslinked sago starch in aqueous solution with respect to solution pH value, adsorbent dosage, initial concentration, contact time and temperature.

Batch adsorption experiments will be carried to optimize the adsorption of dye using the crosslinked sago starch at different operating conditions. In this study the ranges used for the pH are 3 to 10, adsorbent dosage is between 0.02 to 0.2 g, initial concentration is analysed at a range of 2 to 50 ppm, contact time is between 1 to 240 minutes and temperature is investigated in the range between 30 to 60°C based on the previous work and screening process on adsorption capacity performance. The adsorption isotherm is necessary to describe how the interaction between the adsorbate and the adsorbent as well as provide a better understanding about adsorption capacity. In this study, the Langmuir, Freundlich and Tempkin isotherm models are employed to investigate the adsorption isotherm. The adsorption isotherms obtained were used to calculate the thermodynamic parameter.

Further, adsorption kinetics in terms of the order of the rate constant can be used to examine the dynamics of the adsorption. To analyse the experimental data obtained, three different models were applied in order to evaluate the kinetic parameters for the adsorption process which are pseudo-first-order model, pseudo-second order model and intra-particle diffusion based on the effect of adsorption time. A thermodynamic study, with respect of temperature effect where the enthalpy, entropy and Gibbs energy that show the spontaneity, is carried out.

- iii) To assess the reusability of desorbed crosslinked sago starch to readsorb dye efficiently and examine the potential of crosslinked sago starch as an adsorbent.

A desorption process become an essential to be studied for the regeneration of the adsorbent and also the recovery the adsorbed compounds. Besides that, desorption studies also help to describe in details about the adsorption mechanism that occurs. After the desorption study, the performance efficiency of readsorption of dye was analysed. Sago starch adsorbent was then analysed to examine its potential as one of the low-cost adsorbents.

## **1.5 Significance of the study**

A strong persistent colour and high BOD loading by substantial amount of dye wastewater effluent have led to a critical eco-system problem (Cheng *et al.*, 2009). Therefore, the treatment of dyeing effluents becomes the main concern in recent years by many researchers, and various technologies have been approached for removal of dye from the wastewater. The adsorption technique has been favoured

and selected because of it is straightforward and possesses great ability, and finally the feasibility of many types of adsorbents. Choosing a capable adsorbent through adsorption procedure will enhance and provide a good quality treated effluents. Based on the need of effective and capable sorbent to remove coloured wastewater effluent, this proposal has been carried out. Dyes are extensively applied in the textile, food, paper, and pharmaceutical cosmetic industries. It is reported that over  $7 \times 10^5$  metric tons of synthetic dyes are produced annually for industrial application where 5–10% from the amount is directly discharged into the environment along with the wastewater (Janaki *et al.*, 2012).

This research also proposed starch, which is abundant, biodegradable and inexpensive, a natural renewable resource which is extensively used in various areas as a result from a number of good features of its own. Sago starch has attracted much attention to be used as an adsorbent in this research since it is abundant in Malaysia and possesses several other advantages. Poor adsorbing functional groups features present in native starch has caused a restricted capability of dye adsorption (Janaki *et al.*, 2012). Further, in engineering the application of starch is restricted because of the weak physical properties such as mechanical strength, dimensional stability and so forth. To improve it, crosslinking reaction is applied to acquire insoluble, high surface and stable modified starch (Cheng *et al.*, 2009). Several approaches have been made to alter the starch as a potential adsorbent for dyes. However, lesser application in a large scale by modified starch is due to high cost is needed and is not feasible. Therefore, starch based adsorbent is synthesized for the removal of dye from aqueous solution. Thus, in order to achieve an economical and environmental friendly sorbent, crosslinked sago starch will be used in this study.

As a result, it will also keep the environment safe because the used adsorbent will be regenerated and desorb the adsorbed dye to be reabsorbed back as much pollutant as they can. The optimum parameter for crosslinked sago starch will be determined through this research. The cost of sago starch itself was assumed low



and only needed to purchase crosslinking agents in order to enhance the adsorption process. There is no abandoned secondary waste will be produced. Therefore, this research is economic and has an ecological approach. This research can be a reference for commercial and industrial production and application. This study is expected to be a solver to the problem to get the effective sorbent of coloured wastewater nowadays.

## **1.6 Thesis Outline**

The thesis is presented into five main chapters and each chapter explains the sequence of this research. Chapter 1 presents brief overview about the general information and introduction to this research along with the problem statement, research objectives, scopes of research, significance of study, thesis outline and summary of this chapter. Chapter 2 explains the deep view of related knowledge about dye pollutant and the available treatment methods nowadays, the reason why adsorption is the preferable method, the advantages and flaws of available treatment is also reviewed. Moreover, sago starch as a chosen material and its wide application in industrial area also will be discussed. Chapter 3 covers the research methodology where experimental procedures including synthesis of adsorbent, characterizations of adsorbent, adsorption process, and degeneration will be deliberated. Chapter 4 will briefly explain on the result and discussion of this research. Meanwhile, Chapter 5 presents the conclusion of this research and future work recommendations.

## 1.7 Summary

The research background, problem statements, research objectives, scopes of research, the significance of the study and finally the thesis outline are thoroughly presented and explained in this chapter. Generally, this research is conducted in order to remove dye stuff from aqueous solution and which will be implemented in the real solution. Dye as a hazardous contaminant in water which leads to unpleasant effect even if its existence is in a small amount. Thus, the removal of dye will eventually help to curb water contamination where low-cost adsorbent yet effective is employed rather than using the expensive ones. Two solutions will be directly covered in one research which is the water pollution caused by dye contamination as well as the cost reduction in this adsorption process.

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