REMOVAL OF CATIONIC, ANIONIC AND NON–IONIC DYES FROM AQUEOUS SOLUTIONS USING *DURIO ZIBETHINUS* HUSK

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REMOVAL OF CATIONIC, ANIONIC AND NON–IONIC DYES FROM AQUEOUS SOLUTIONS USING *DURIO ZIBETHINUS* HUSK

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A thesis submitted in fulfilment of the requirement for the award of the degree of Master of Engineering (Chemical)

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This thesis is dedicated to whom I love
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ABSTRACT

Development of economical adsorbents from peanut hull, hazelnut shell, bottom ash and other waste materials to treat dyes in wastewater attracts a great interest in recent years. However, the adsorption capacities of these materials are still limited. Economical, locally available and highly effective adsorbents are still under investigation. The purpose of this study is to investigate the potential of *Durio zibethinus* husk (*DZH*) as a low–cost adsorbent to remove cationic dye, Malachite Green (MG): anionic dyes, Congo Red (CR) and Reactive Blue 221 (RB 221): and non–ionic dyes, Disperse blue 60 (DB 60) and Disperse violet 93 (DV 93) from aqueous solution. Adsorption studies were carried out under various parameters including adsorbent pre‒treatment, contact time, pH (2–11), amount of adsorbent (0.25‒7.5 g/L), initial concentration (10‒200 mg/L) and temperature (30‒50 °C). Results revealed that the pre‒treatment of *DZH* and pH have significant effect on the removal of dyes. MG reached its maximum removal percentage of 76% using untreated *DZH*. However, maximum removal percentage of other dyes were obtained using treated *DZH*, i.e., 62,70,99 and 79% for CR, RB 221, DB 60 and DV 93, respectively. The adsorption data were correlated using Langmuir and Freundlich models, and the result showed that all dyes fitted well with the Langmuir model. The kinetic data were analyzed using pseudo ‒first‒and pseudo‒second‒order equations, and all dyes studied conformed to the pseudo‒second‒order kinetic model. The intraparticle diffusion model indicated that multiple stages were involved in the adsorption process. Negative value of ΔH for CR, RB 221 and DV 93 confirmed the exothermic nature of adsorption process, while the positive values for MG and DB 60 showed the endothermic adsorption in nature. So the conclusion,
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<tr>
<td>$\beta$</td>
<td>Beta</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$C_o$</td>
<td>Initial concentration</td>
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<tr>
<td>$C_e$</td>
<td>Equilibrium concentration</td>
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<td>$C_{AE}$</td>
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<td>$C_{SE}$</td>
<td>Equilibrium concentration (mg/L) of the dye in the solution</td>
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<tr>
<td>$%$</td>
<td>Removal percentage</td>
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<tr>
<td>$^\circ C$</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$G$</td>
<td>Gram</td>
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<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
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<td>$\Delta H$</td>
<td>Enthalpy</td>
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<td>$K$</td>
<td>Kelvin</td>
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<td>$K_L$</td>
<td>Amount of adsorbate required to form a monolayer</td>
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<td>$K_f$</td>
<td>Freundlich constant</td>
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<td>$K_c$</td>
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<td>$k_p$</td>
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<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>Min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mg/L</td>
<td>Milligram per Liter</td>
</tr>
<tr>
<td>mg/g</td>
<td>Milligram per gram</td>
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<tr>
<td>$q_{max}$</td>
<td>Maximum adsorption capacity</td>
</tr>
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<td>$q$</td>
<td>Adsorption capacity</td>
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<tr>
<td>$R^2$</td>
<td>Correlation coefficients</td>
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<td>Symbol</td>
<td>Description</td>
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<td>----------------------</td>
</tr>
<tr>
<td>( R_L )</td>
<td>Dimensionless constant</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>Entropy</td>
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<tr>
<td>( T )</td>
<td>Temperature</td>
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<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>CAC</td>
<td>Commercial activated carbon</td>
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<tr>
<td>CR</td>
<td>Congo Red</td>
</tr>
<tr>
<td>CI</td>
<td>Color index</td>
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<td>DB 60</td>
<td>Disperse Blue 60</td>
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<td>DV 93</td>
<td>Disperse Violet 93</td>
</tr>
<tr>
<td>DZH</td>
<td><em>Durio zibethinus</em> Husk</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transforms Infrared</td>
</tr>
<tr>
<td>FESEM</td>
<td>Electrons in Field Emission Scanning Electron</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>MG</td>
<td>Malachite Green</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
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<td>RB 221</td>
<td>Reactive Blue 221</td>
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<td>UV–vis</td>
<td>Ultraviolet–visible</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction

Synthetic dyes are widely used in many industries including textiles, rubber, paper, plastics, cosmetics, food and etc. The effluent of these industries is well known pollutants to the receiving bodies in the surrounding areas. Color of the dyes is the first contaminant to be recognized since it is visible to the human eye. Even the presence of dyes at concentrations as low as 1 ppm could be highly visible and affected the quality of water bodies (Banat et al., 1996).

Dyes in wastewater can cause serious problems to the human and environment such as toxicity, mutagenic and carcinogenic effects, biodegradation, light penetration and photosynthesis (Caparkaya and Cavas, 2008). It also contributes appreciable concentrations of material with high chemical and biological oxygen demands, suspended solids and content in toxic compounds (Aksu, 2005). Therefore, the most effective, simple and economic treatment of such wastewater containing soluble dyes is required for complete and secure disposal.
Various techniques have been employed for the removal of dyes from wastewater such as adsorption (Santhy and Selvapathy, 2006), coagulation (Mohan, et al., 1999), membrane filtration (Fersi et al., 2005), chemical oxidation (Sarasa, et al., 1998) and etc. Among these methods, adsorption is the most popular one due to its efficiency, simplicity of design and applicability on large scale for treating dyes with more concentrated form.

Currently, the most commonly used adsorption agent in industry is activated carbon which has been proven to be an effective adsorbent but its production and regeneration are expensive processes. However, relatively high operating costs and problems with regeneration of the spent carbon hamper its large scale application. In this respect, these have led many researches to investigate other alternative low–cost and easily available material for the adsorption of dyes.

Biomass can be promising potential alternative to conventional used adsorbent for the removal of dyes since it involves several complex mechanisms such as surface adsorption, ion exchange, complexation and micro precipitational. Nowadays, several studies have been conducted using agricultural by–product as a low–cost adsorbent such as de-oiled soya (Gupta et al., 2006), activated date pits (Banat et al., 2003), wood (Ofomaja and Ho, 2008.), rice husk (Malik, 2003), fly ash (Viraraghavan and Ramakrishna, 1999) and cedar sawdust (Hamdaoui, 2006). However, abundance, locally available and low–cost adsorbent are still needed for industrial scale.

*Durio zibethinus* is well known as *durian* is the fruit of several tree species belonging to the genus *Durio* and the Malvaceace family (Brown, 1997). Widely, known and revered in Southeast Asia as the ‘king of fruits’, the durian is distinctive for its large size, unique odour and formidable thorn covered husk. According to the FAO online databases, it is estimated that Malaysia produced 245 000 tonnes of *durian* in 2001. However, due to high consumption of durian in the country, massive of amount of husk wastes were disposed which can cause a severe environmental
problem. Therefore herein, a potential usefulness of *durian* husk as an inexpensive solid adsorbent for removal cationic, anionic and non-ionic dyes has been demonstrated in this studied.

### 1.2 Problem Statement

Few decades earlier, the dyes selection, application and use were not given a major consideration with respect to their environmental impact. Even the chemical composition of half dyes used in the industry was estimated to be unknown. However, disposal of dyes in precious water resources must be avoided and for that various treatment technologies are in use. Among various methods adsorption occupies a prominent place in dye removal.

The growing demand for efficient and low–cost treatment methods and the importance of adsorption has given rise to adsorbents. Several studies have proven that agricultural by–product which are low–cost materials were successfully applied in the removal of dye from aqueous solution (Mohd et al., 2010). Because of low utilization ratio, most of these bio–materials are randomly discarded or set on fire. These disposals must result in resource loss and environmental pollution. The exploitation and utilization of these biomaterials must bring obvious economic and social benefits to mankind. In recent years, attention has been focused on the utilization of native agricultural by–products as sorbent (Marshall, 1993; Marshall and John, 1996; Namasivayam, et al., 1996; Robinson, 2002; Gong, 2005a,b). Most of these by–products are considered to be low value products. Chemical modification has shown great promise in improving the cation exchange capacity of agricultural waste by–products (Laszlo and Dintzis, 1994; Marshall and Johns, 1996; Marshall et al., 1999)
In this study, *durian* husk was used as an alternative low–cost adsorbent since it abundantly produced especially in producing processed product. Durian husk principally consist of cellulose, hemi–cellulose, lignin and other low molecular weight hydrocarbon (Khedari et al., 2003). Cellulose could be a very promising raw material for the preparation of various functional polymers. Many investigators have done much work on the modification of cellulose in order to prepare a novel, effective and alternative material. (Akelah and Moet, 1990; Liu 2000; Shukla and Shakarnade, 1991; Wang et al., 1998). These components contain various functional groups, such as carbonyl and hydroxyl (Al–Ghouti et al., 2010), which make durian husk to be a potential adsorbent material for removing cationic, anionic and non–ionic dyes from aqueous solution. Durian husk is expected to have a great potential to be good adsorbents, which not only can solve environmental pollution but also give advantages from an economic point of view.

1.3 **Objectives of Research**

The objectives of this research are:

i. To study the chemical and physical properties of *DZH* for better understanding of its behavior in sorption of dyes.

ii. To investigate the optimum conditions of the cationic, anionic and non–ionic dyes removal from aqueous solution in order to found the maximum adsorption capacity of those dyes.

iii. To study the equilibrium isotherms, kinetics and thermodynamics of the adsorptions in order to identify the details of the type of the adsorption.
iv. To study the proposed mechanism of adsorption of each dyes onto the untreated and treated \textit{DZH}.

1.4 Scopes of Research

The main scopes of this study are:

i. Study the chemical and physical properties of \textit{DZH} by Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FE–SEM).

ii. Investigate the optimum conditions of removal of cationic dye, Malachite green (MG); anionic dyes, Congo red (CR) and Reactive blue 221 (RB 221); and non–ionic dyes, Disperse blue 60 (DB60) and Disperse violet 93 (DV 93) from aqueous solution through adsorption batch studies under various parameters such as, effect of pre–treatment adsorbent (HCl chemical), contact time (60–120 min), pH (2–11), concentration adsorbent (0.25–7.5 g/L), initial concentration (10–200 mg/L) and temperature (30–50 °C).

iii. Study the equilibrium isotherms by the Langmuir and Freundlich isotherms models. The Pseudo–first–order, Pseudo–second–order and intraparticle diffusion were applied to the experimental data in order to clarify the adsorption kinetics of dyes onto adsorbents. The thermodynamic parameters of the adsorptions of each dye including the change of Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were calculated using Van’t Hoff equation.
iv. Study the proposed mechanism of the adsorption of each dye onto untreated $DZH$ (MG) and treated $DZH$ (RB 221 and DB 60) by using FTIR spectroscopy.

1.5 Thesis Outline

This study consists of five chapters, which present the research in sequential order. Chapter 1 introduces the research background, problems statement, objectives, scopes, and significant of this research. Chapter 2 reviews the literatures those related to cationic, anionic and non-ionic dyes and current issues about the adsorption process. Chapter 3 describes the experimental procedures and characterization of the adsorbents whereas Chapter 4 analyzes and discusses the characterization and experimental data. Finally, the conclusion and recommendation for future were presented in Chapter 5.

1.6 Significant of Research

The use of the $DZH$ as an adsorbent for dye removal is of a great attention since it is an agricultural by–product, abundance and locally available. The potential of the $DZH$ to remove cationic, anionic and non-ionic dyes was studied under various parameters such as effects of adsorbent pre–treatment, contact time, pH, adsorbent dosage, initial concentration and temperature in order to obtain the optimum conditions of the adsorption. This finding would be beneficial not only from economy aspects but also from an environmental point of view.
REFERENCES


