ADSORPTION OF RHODAMINE B BY METALS CHLORIDE-ACTIVATED CASTOR BEAN RESIDUE CARBON

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UNIVERSITI TEKNOLOGI MALAYSIA
ADSORPTION OF RHODAMINE B BY METALS CHLORIDE-ACTIVATED CASTOR BEAN RESIDUE CARBON

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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Philosophy

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Special dedicated to my beloved father and mother.
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ABSTRACT

Zinc chloride (ZnCl\textsubscript{2}) is a well-known pollutant which is toxic to the aquatic organisms. A study of adsorption of rhodamine B was conducted to investigate the performance of metals chloride activated carbon prepared from castor bean residue. Rhodamine B was selected as the model dye due to its high stability with change in pH and hazardous properties. Castor bean residue is suitable to be used as precursor to replace conventional activated carbon due to its low cost and high carbon content. The preparation of activated carbons was conducted through impregnation with ZnCl\textsubscript{2}, potassium chloride, magnesium chloride, ferric chloride and metals chloride composite at various impregnation ratios from 0.5 to 2.5. Activated carbons were characterized based on proximate analysis, elemental analysis, textural characteristics and chemical properties. The adsorption data were analysed using isotherm models, kinetics models and thermodynamics properties. The regeneration of activated carbon was carried out by hot water and irradiated water at three regeneration cycles. The specific surface area of activated carbons of ratio 1.0 are in descending order of potassium chloride (KCBR-1.0), ferric-zinc chloride (FZCBR), magnesium-zinc chloride (MZCBR), zinc chloride (ZCBR-1.0), ferric chloride (FCBR-1.0), potassium-zinc chloride (KZCBR), magnesium chloride (MCBR-1.0). ZCBR-1.0 demonstrated a greater rhodamine B adsorption of 175 mg/g compared to the other activated carbons counterparts. Nevertheless, the composite activated carbons, MZCBR and FZCBR displayed adsorptive capacity of 114 and 115 mg/g, respectively, which indicates the mixtures of less hazardous metal chloride salts as the promising activating agents. The adsorption capacity of rhodamine B by activated carbons of ratio 1.0 are in descending order of ZCBR-1.0, FZCBR, MZCBR, FCBR-1.0, MCBR-1.0, KCBR-1.0, KZCBR. Adsorption mechanism of ZCBR-1.0 obeyed Langmuir isotherm and pseudo-second-order kinetics model. The rate-limiting step in the adsorption of rhodamine B is film diffusion. The positive values of enthalpy change and entropy change indicate of that the adsorption process is endothermic and spontaneous at high temperature. Hot water regeneration onto rhodamine B loaded activated carbon showed a better performance with 37.7 % regeneration efficiency and 34.4% recovery.
ABSTRAK

Zink klorida (ZnCl₂) adalah pencemar toksik kepada organisma akuatik. Satu kajian penjerapan rhodamine B telah dijalankan untuk mengkaji prestasi karbon teraktif daripada sisa kacang kastor dengan pengaktifan logam klorida. Rhodamine B dipilih sebagai model pencelup kerana kestabilannya yang tinggi terhadap perubahan pH dan sifat-sifat berbahaya. Sisa kacang kastor sesuai digunakan sebagai prapananda untuk menggantikan karbon teraktif lazam kerana ia murah dan mempunyai kandungan karbon yang tinggi. Penyediaan karbon teraktif dikendalikan melalui impregnasi dengan ZnCl₂, kalium klorida, magnesium klorida, ferik klorida dan komposit logam klorida pada pelbagai nisbah impregnasi dari 0.5-2.5. Karbon teraktif dicirikan berdasarkan analisis hampiran, analisis unsur, ciri-ciri tekstur dan sifat-sifat kimia. Data penjerapan dianalisis dengan model isoterma, model kinetik dan sifat termodinamik. Penjanaan semula karbon teraktif dengan air panas dan air teriradiasi dijalankan pada tiga kitaran penjanaan semula. Luas permukaan tentu karbon teraktif dengan nisbah 1.0 adalah mengikut tertib menurun kalium klorida (KCBR-1.0), ferik-zink klorida (FZCBR), magnesium-zink klorida (MZCBR), zink klorida (ZCBR-1.0), ferik klorida (FCBR-1.0), kalium-zink klorida (KZCBR), magnesium klorida (MCBR-1.0). ZCBR-1.0 memberikan prestasi penjerapan rhodamine B lebih tinggi dengan 175 mg/g berbanding dengan karbon teraktif yang lain. Walaubagaimanapun, karbon teraktif komposit, MZCBR dan FZCBR masing-masing memberikan kapasiti jerapan 114 and 115 mg/g yang menunjukkan pengaktifan campuran garam logam klorida kurang berbahaya sebagai agen pengaktifan yang berpotensi. Kapasiti penjerapan rhodamine B oleh karbon teraktif dengan nisbah 1.0 adalah mengikut tertib menurun ZCBR-1.0, FZCBR, MZCBR, FCBR-1.0, MCBR-1.0, KCBR-1.0, KZCBR. Mekanisma penjerapan ZCBR-1.0 mematuhi model isoterma Langmuir dan model kinetik pseudo-tertib kedua. Langkah kadar-penghad dalam penjerapan rhodamine B ialah resapan filem. Nilai-nilai positif perubahan entalpi dan perubahan entropi menunjukkan bahawa proses penjerapan adalah endotermik dan spontan pada suhu tinggi. Penjanaan semula karbon teraktif terjerap rhodamine B menggunakan air panas menunjukkan prestasi lebih baik dengan kecekapan penjanaan semula 37.7% dan perolehan 34.4%.
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<td>Activated carbon</td>
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<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
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<td>C</td>
<td>Carbon</td>
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<tr>
<td>CaCl₂</td>
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<td>CBR</td>
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<td>Fe³⁺</td>
<td>Ferric ion</td>
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<td>Fe₂O₃</td>
<td>Ferric oxide</td>
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<td>FESEM</td>
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<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
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<td>RB</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>RE</td>
<td>Regeneration efficiency</td>
</tr>
<tr>
<td>R²</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>Rₗ</td>
<td>Equilibrium parameter</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UTM</td>
<td>Universiti Teknologi Malaysia</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>Zinc chloride</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>∆H₀</td>
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</tr>
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CHAPTER 1

INTRODUCTION

1.1 Research Background

Industrialization is a main key to the economic development, but it is also the root cause of environmental issue. In Malaysia, textile production is not just a fashion trend, but it is also known as the artistic legacy. However, due to the high customer demand, and improper industry effluent management, dye pollution has been a serious threat to the public health and the environment. Therefore, dye wastewater treatment issues must be faced up.

Dye is a visible pollutant. It existence affects not only the quality of surface water, but also changes the aquatic ecosystems as well as reduces the light penetration. Dyes can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnoea, irritation to the skin, and if ingested, may lead to irritation to the gastrointestinal tract, nausea, vomiting and diarrhea (Senthikumaar et al., 2005).

There are various treatment methodology have been investigated such as biodegradation, coagulation, oxidation, adsorption and so on. Adsorption is the most economical attractive due to the flexibility and simplicity of design, ease of operation
and insensitivity to toxic pollutants (Robinson et al., 2001; Gupta and Suhas, 2009). This process creates a film of adsorbate on the surface of the adsorbent. Besides, when compared with other physico-chemical treatment methods, adsorption is more inexpensive and does not produce sludge (Demirbas et al., 2008). Activated carbon is widely used as adsorbent for dye adsorption due to its large porous surface area, controlled pore structure and inert properties (Walker and Weatherley, 1997).

Activated carbon can be prepared from a variety of raw materials, especially agricultural by-products such as coconut shells, used tea leaves, orange peels and so on (Hu and Srinivasan, 1999; Arami et al., 2005; Tahir et al., 2009). These products are regarded as waste and can caused serious disposal problem in some countries. Therefore, converting them into activated carbon is a feasible solution to the environmental problem. In this study, castor bean residue was used as the precursor of activated carbon.

Malaysia is situated in tropical zone with enough rain and sunlight that suit to castor plant. Castor oil derivatives are similar to petroleum derivatives, thus it is a perfect alternative to petroleum. Furthermore, there is a huge potential for castor oil to be used as biodiesel for vehicle. By year 2015, the global demand for castor oil is estimated to be around 2 million tons. Castor bean residue is the by-product of biodiesel production which remains after the extraction of the oil and comprises about 50% of the weight of castor bean (Robb et al., 1974), which is 1.1 tons per every 1 ton of castor oil production (Santos et al., 2014). Moreover, castor bean residue has no viable application as it contains ricin, a protein that is toxic to cattle (Madeira et al., 2011). Due to its abundant source, castor bean residue is seen as a suitable candidate to replace the conventional precursor of activated carbon.

The preparation of activated carbon via chemical activation involves the use of activating agents such as K$_2$CO$_3$, ZnCl$_2$ or KOH. During pyrolysis of cellulose, an organic compound with six carbon ring structure known as levoglucosanis formed, and results in the formation of tar. Some of the pores on carbon are filled or partially
blocked by tars and consequently its adsorption capacity becomes lower. Activating agents are functioned as dehydrating agents to inhibit the formation of tar during the pyrolytic decomposition (Derbyshier et al., 1995). Hence, higher yield and better development of porosity are always found in the case of chemical activation when compare to the physical activation. Moreover, lower activation temperature and shorter time are required for chemical activation process (Lim et al., 2010). Zinc chloride ($\text{ZnCl}_2$) is a well-known activating agent in the synthesis of activated carbon for wastewater treatment. However, zinc cation is a well-known pollutant in aqueous solution. It is toxic to the aquatic organism and may cause long-term adverse effects to the aquatic environment. So, less hazardous metals chloride salts were investigated in this study to replace $\text{ZnCl}_2$ as activating agent.

1.2 Problem Statement

$\text{ZnCl}_2$ is a widely used activating agent in the preparation of activated carbons for research, but there are concerns about the aquatic toxicity of $\text{ZnCl}_2$ in large-scale manufacturing process. Because it is a powerful Lewis acid, zinc cation in aqueous solution gives corrosive effect to bacteria, plants, invertebrates and vertebrate fish. Zinc toxicity may take months to resolve because there is no particular body store for zinc when it dissolves in HCl in stomach (Nriagu, 2007). Less toxic metals chloride such as $\text{KCl}$, $\text{MgCl}_2$ and $\text{FeCl}_3$ have similar characteristics to $\text{ZnCl}_2$ in aqueous solution, which opens up the possibility of replacing $\text{ZnCl}_2$ as activating agent in the preparation of activated carbon (Rufford et al., 2010).
1.3 Objective

Three objectives in this research are stated below:

i. To synthesize and characterize activated carbons from castor bean residue by different metals chloride salts activation.

ii. To establish the adsorptive studies of rhodamine B by activated carbons at different initial concentrations, time intervals and temperatures.

iii. To evaluate the regeneration of spent-activated carbon using hot water and irradiated water for three consecutive cycles.

1.4 Scope of Study

i) To synthesize and characterize activated carbons prepared from castor bean residue by different metals chloride salts activation.

Impregnation was carried out using metals chloride salts as activating agents, which are ZnCl₂, KCl, MgCl₂, FeCl₃ and composites of metal chloride salts at various impregnation ratios from 0.5 to 2.5. Heating temperature and heating period were fixed at 550°C and 1.5 h, respectively. Activated carbons were characterized based on specific surface area, morphology, surface functional group, Boehm titration and elemental analysis.

ii) To establish the adsorptive studies of rhodamine B by activated carbons at different initial concentrations, time intervals and temperatures.
The studies were carried out for the best-performed activated carbons from each activation series. Rhodamine B was used as adsorbate model. Four isotherm models which are Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich were used to fit the adsorption data at different initial concentrations. Rate of adsorption for three initial concentrations at different time intervals was evaluated using the pseudo-first order equation, pseudo-second order equation, intraparticle diffusion model and Boyd model. The thermodynamics properties, name by Gibbs energy, $\Delta G^\circ$, enthalpy, $\Delta H^\circ$ and entropy, $\Delta S^\circ$ were investigated through the effect of temperature on dye adsorption from 20 to 55°C for the best-performed activated carbon.

iii) Regeneration of spent-activated carbon using hot water and irradiated water.

The regeneration study was performed using hot water and irradiated water for three consecutive adsorption-desorption cycles to determine the regeneration efficiency and recovery of activated carbon.

1.5 Significance of Study

This study is carried out to give further understanding on the contribution of agricultural waste activated carbon to dye-containing wastewater treatment. The issues related to castor bean waste management can be reduced if it is converted into activated carbon. Less-toxic activating agents are investigated as an alternative to ZnCl$_2$ in the preparation of activated carbon for dye removal. This study also proposes an environmental friendly approach for regeneration method of spent activated carbon.
REFERENCES


LIST OF PUBLICATIONS


