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博 士 論 文

農業廢棄物衍生之吸附劑對去除水中陽離子染料、抗生素、重金屬等污染物之應用

Application of sorbents derived and converted from agricultural wastes in removal of cationic dye, antibiotic, and heavy metal pollutants from aqueous solution

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The author of this thesis is qualified for a Doctoral degree through the verification of the committee.

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摘要

近年來由於工業化及人口增長等因素，許多開發中國家開始面臨日益嚴重的環境污染問題，包括有害物質對水源所造成的污染。而在水和廢水處理工法中，吸附一向被認為是成本相對較低且有效的方法，因此受到發展中國家的青睞，常用於去除受污染水源中有害、不可生物降解的污染物。在越南，由於農業仍在經濟上扮演著至關重要的角色，因此可將農業活動所衍生的大量農廢視為寶貴的原料，以合成碳吸附劑並應用在污染整治。儘管農廢合成的吸附劑常以活性炭（AC）為優先選擇，但傳統的 AC 在合成時常涉及高溫（600 - 1200 °C）的碳化和活化程序，反讓 AC 被視為是昂貴且較不環保的材料，故需開發更簡單、更綠色、更完善的方法合成碳基吸附劑，且能有效地應用於污染處理。水熱合成炭（HC）即是近期極受關注的碳屬吸附材，因為這種碳質材料是通過低溫（180 - 350 °C）的水熱碳化製備而來，因此可保有表面氧化官能基的豐富度。本研究即試著利用農業廢棄物以水熱法合成低成本的吸附劑，並在適當的改質下探討這些吸附劑用於去除水中典型的離子污染物，如陽離子染料（以亞甲基藍(MB)作為模擬化合物）、抗生素（以四環素(TC)作為目標藥物）以及金屬物種（以 Cu^{2+}，Cd^{2+} 作為測試離子）的可行性及背後的吸附機制。

在進行吸附試驗之前，所有合成吸附劑均通過 SEM、S_{BET} 分析儀、FTIR、XPS 技術和 Boehm 滴定(用以確定酸性官能基團)進行表徵。首先，經由廢棄的橙皮合成出水熱合成炭（原始水熱合成炭），然後再用硝酸對其進行改質（氧化水熱合成炭）用以吸附 MB。結果表明，由 Langmuir 模型估算出 30 ºC 時

的 MB 最大吸附容量依序為 mGH (246 mg/g) > mOPH (107 mg/g) > OPH (59.6 mg/g) > GH (54.8 mg/g)。再來，使用柚木鋸末通過水熱碳化後，然後用不同濃度的 $ZnCl_2$ 或 K_2CO_3 進行化學活化來合成 AC。ACs 對於污染物 MB、Cd(II)和 Cu(II)的吸附能力隨使用活化劑的濃度而增加：當碳質材料與 $ZnCl_2$ 的重量比達到 1.75 時，可實現出最大的吸附能力。 MB、Cd(II) 和 Cu(II) 的最大吸附容量分別為 516 mg/g，166 mg/g, 和 159 mg/g。最後，由於 TC 是一種 pH 可調的化合物，因此可用來驗證先前測試得出具有較高吸附容量的 HC 和 AC 材料之吸附途徑。由 Langmuir 模型估算出 TC 在 25 ºC 和 pH 5.5 條件下的最大吸附容量遵循以下順序：ACZ1175 (257.28 mg/g) > mGH (207.11 mg/g) > WAC (197.52 mg/g) > mOPH (168.50 mg/g) > OPH (85.79 mg/g) > GH (75.47 mg/g)。 此外，這項研究的潛在吸附機制以靜電吸引力被認為是導致被測污染物吸附到樣品上的主要途徑；再著，π-π 和 n-π 相互作用成為 MB 和 TC 吸附到氧化水熱合成炭上的次要途徑，而且錯合反應是導致 AC 與金屬(Cu^{2+}、Cd^{2+})之間相互作用的重要吸附機制；不僅如此，結果表明含氧官能基團的數量多寡被認為是確定吸附量的重要因素。

本研究的實驗結果及廣泛探討所獲得的知識，預期對於進一步開發作為實場應用的低成本材料將有所幫助。

關鍵詞：農業廢棄物；水熱合成炭；活性炭；染料和四環素；重金屬；吸附性

Abstract

Due to the industrialization and population growth in recent years, Vietnam and other developing countries have begun to face problems of increasing environmental pollution, including water contamination with hazardous substances. Of water and wastewater treatment methods, adsorption is considered a relatively low-cost and effective means favored by developing countries for the removal of harmful, non-biodegradable pollutants from contaminated water. Because agriculture still plays a vital role in the economy of Vietnam, it becomes clear that the abundance of agricultural wastes can be valuable feedstocks of carbonaceous sorbents used for pollution handling in Vietnam. While activated carbon (AC) derived from agricultural residues has been used as a preferential sorbent in this regard, the traditional way of AC synthesis involving processes of carbonization and activation under high-temperature (600–1200 °C) conditions makes AC an expensive, eco-unfriendly material. Hence, there is a need for the development of carbon-based adsorbents via a simpler, greener, and robust way for effective use in dealing with pollution. Recent attention has been drawn to hydrochar (HC), as this carbonaceous material is prepared through hydrothermal carbonization at low temperature (180–350 °C) and thus the richness of surface oxygenated functionality can be maintained. This study thus explores the potential of low-cost adsorbents derived from agricultural wastes in removal of typical ionic contaminants such as cationic dyes (using methylene blue, MB, as the model compound), antibiotics (tetracycline, TC, as the targeted drug), and metal species (Cu^{2+}, Cd^{2+} as the tested ions) from aqueous solution.

Prior to adsorption tests, all synthetic sorbents were characterized through the SEM, S_{BET} analyzer, FTIR, XPS techniques, and Boehm titration to determine the acidic functional groups. First, hydrochars were derived from wasted orange peels (raw-hydrochars) and further modified with nitric acid (oxidized-hydrochars) to adsorb MB. Results show that the maximum MB adsorption capacity at 30 ºC estimated by the Langmuir model followed by

the order of mGH (246 mg/g) > mOPH (107 mg/g) > OPH (59.6 mg/g) > GH (54.8 mg/g). Second, teak sawdust was used to synthesize ACs through hydrothermal carbonization followed by chemical activation with varying concentrations of $ZnCl_2$ or K_2CO_3. For ACs, their MB-, Cd(II)-, and Cu(II)-adsorption capacity increased with the concentration of the activating agent: the maximum adsorption capacities were achieved when the weight ratio of the carbonaceous material to $ZnCl_2$ reached 1.75. The maximum adsorption capacities obtained for MB, Cd(II), and Cu(II) were 516 mg/g, 166 mg/g, and 159 mg/g, respectively. Finally, because TC is a pH-tunable compound, it was used to validate the adsorption pathways concluded from prior tests with those higher adsorption capacity-HC and AC materials. The maximum adsorption capacities of TC estimated by the Langmuir model were found to follow the order: ACZ1175 (257.28 mg/g) > mGH (207.11 mg/g) > WAC (197.52 mg/g) > mOPH (168.50 mg/g) > OPH (85.79 mg/g) > GH (75.47 mg/g) at 25 ºC and pH 5.5. In addition, potential adsorption mechanisms were deeply discussed in this study. The electrostatic force was identified as the primary pathway that led to the adsorption of the tested contaminants onto the sample. Further, while the π-π and n-π interaction became minor pathways for MB and TC adsorption onto oxidized-hydrochars, the complexation reaction was an important mechanism responsible for the adsorptive interaction between ACs and metal species (Cu^{2+}, Cd^{2+}). Moreover, the result illustrated that the amount of oxygen-containing functional groups is regarded as an important factor in determining the adsorptive amounts.

It is expected that the knowledge obtained through extensive exploration in this study would help further development of the low-cost materials for the practical applications.

Keywords: Agricultural wastes; Hydrochars; Activated carbons; Dyes and Tetracycline; Heavy metals; Adsorption

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