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著者(和文)	LEQuang Huy
Author(English)	Quang Huy Le
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Le Quang Huy
Student's Name

指導教員（主）： Yusuke Shimoyama
Academic Supervisor(main)

指導教員（副）：
Academic Supervisor(sub)

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This Doctoral dissertation introduces a novel wastewater treatment technique, called "CO_2-activated system". The thesis is divided into 5 chapters. Chapter 1 provides an introduction to this research. This includes research background, motivation and objectives. A detailed literature review is included, which discusses existing wastewater technologies, development of adsorption technique over the years, common adsorbents and existing CO_2-activated separation systems. Compared with other techniques, adsorption in CO_2-activated separation system is expected to provide an environmentally-friendly and effective way of treating wastewater pollutants. The utilization of CO_2 is also non-toxic, easily reversible and contributes to the alleviation of global warming.

In chapter 2, the thesis focuses on the application of CO_2-activated for the removal of dyes. Adsorption of 3 anionic dyes: Brilliant Blue FCF (BBF), Congo Red (CR), Orange II (O-II) and 1 cationic dye: Crystal Violet (CV) was conducted on chitosan hydrogel in CO_2-activated system. In this chapter, three major breakthrough results were discovered. First of all, CO_2 was found to be capable of improving chitosan's adsorption capacity significantly by the protonation of amino groups on chitosan molecules. The high adsorption capacity and rapid dye adsorption behaviour was achieved with the protonated chitosan structure. Secondly, CO_2 activation was found to enhance chitosan's stability by a carbamate cross-link formation between chitosan and CO_2 at elevated temperatures higher than 45°C. Thirdly, the chemical structure of dyes was also found influence adsorption performance. Adsorption of CV, a cationic dye, could not be adsorbed on CO_2-activated chitosan due to the repulsive electrostatic interaction. On the other hand, adsorption of anionic dyes could be significantly enhanced by the electrostatic attraction between dyes' sulfonic groups and CO_2-activated chitosan's protonated amino groups.

In chapter 3, a hybrid CO_2-activated system is proposed for the removal of a pharmaceutical compound (Diclofenac, DCF). The hybrid system consists of CO_2-activated precipitation and CO_2-activated adsorption. In

the precipitation step, CO_2 was utilized to activate solubility reduction, which could rapidly reduce DCF's concentration to less than 5 mg L^{-1}. Low temperature was found to increase the precipitation efficiencies, while the rapid precipitation of DCF in CO_2-activated system could be achieved at a high DCF initial concentration and high CO_2 flow rate. In the adsorption step, CO_2 was utilized to activate DCF for adsorption on chitosan hydrogel, multi-walled carbon nanotube and carbon nanofiber. While adsorption on chitosan was not effective, carbon nanofiber and carbon nanotube showed high removal efficiency of up to 97.6 % and 95.0 %, respectively. The efficient adsorption performance on carbon-based adsorbents was found to come from the electrostatic attraction between the protonated $-NH_3^+$ groups of the drug and the π-electron on the aromatic rings of the carbon-based absorbents. The CO_2-activated adsorption of DCF on carbon nanofiber could also reduce DCF concentration down to 0.115 mg L^{-1}, which is within the safety limit for aquatic species.

Chapter 4 focuses on the kinetics and isotherm modelling of two adsorption processes: CO_2-activated adsorption of dyes on chitosan and CO_2-activated adsorption of DCF on carbon materials. Pseudo-first-order and pseudo-second-order models were evaluated using non-linear regression method. For dye adsorption on chitosan, adsorption was found to follow pseudo-first-order model. Activation by CO_2 was found to lead to a higher adsorption rate constant and a higher adsorption capacity due to the protonation of chitosan's amino groups. Interestingly, as temperature of CO_2-activated system increased, pseudo-first-order model predicted a decrease in adsorption rate constant. This is thought to be a result of lower CO_2 dissolution, which leads to a slower protonation process of chitosan's adsorption sites. Furthermore, both the effects of dye's ionic structure were found to influence adsorption kinetics. It was found that having more charged functional groups would enhance adsorption kinetics due to a more rapid alignment of dye molecules onto adsorption sites. In terms of adsorption isotherm, CO_2-activated adsorption of BBF on chitosan was found to follow Langmuir model with Q_{max} of 1862.2 mg g^{-1}. For adsorption of CO_2-activated DCF on carbon materials, the following points can be concluded. First of all, DCF adsorption on CNT follows pseudo-second-order model, while DCF adsorption on CNF follows pseudo-first-order model. This is due to the significantly bigger pore size of CNF compared with CNT, which allows a direct and easy access of DCF molecules. For adsorption of DCF on CNT, CO_2-activated separation system has a lower adsorption rate constant than pure water, which is due to the effects of CO_2-activated precipitation while adsorption is taking place. For adsorption of DCF on CNF in CO2-activated condition, there is a sudden jump of adsorption capacity, which reaches equilibrium at only 15 min. This jump could be due to the combined contributions of large pore size, strong electrostatic attraction and π-π interaction between DCF molecules and CNF's carbon rings.

In the final chapter, a summary of main results and a future outlook of CO_2-activated system is given based. The final chapter is followed by a list of references, a list of awards, publications in academic journals and presentations during my Doctoral program. A nomenclature is also attached, which includes all the symbols and abbreviations used in this dissertation.