論文 / 著書情報
Article / Book Information

題目(和文)	Carbon dioxide-activated separation system for wastewater treatment
Title(English)	Carbon dioxide-activated separation system for wastewater treatment
著者(和文)	LEQuang Huy
Author(English)	Quang Huy Le
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11159号, 授与年月日:2019年3月26日, 学位の種別:課程博士, 審査員:下山 裕介,関口 秀俊,久保内 昌敏,多湖 輝興,森 伸介
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11159号, Conferred date:2019/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Thesis outline (for Doctoral dissertation)

CARBON DIOXIDE-ACTIVATED SEPARATION SYSTEM FOR WASTEWATER TREATMENT

Le Quang Huy

Academic Supervisor: Prof. Yusuke Shimoyama

Department of Chemical Science and Engineering, Tokyo Institute of Technology, Japan

Chapter 1: Introduction

In this work, we introduced a novel CO_2 utilization technique for the treatment of dyes and pharmaceutical wastewater by adsorption technology. Chapter 1 of the dissertation provided an overall introduction to the research story including the research background, motivation and objectives. In terms of background, the current state of global wastewater treatment was firstly introduced, followed by an explanation of a standard wastewater treatment process, which consists of primary, secondary and tertiary steps. Although many wastewater treatment techniques are currently available, there are still many disadvantages especially at the tertiary treatment step. Most currently available tertiary techniques either uses toxic chemicals or requires further downstream treatment, thus there is a need for the development of an effective and environmentally-friendly technique. Recently, the utilization of CO_2 has been applied successfully in many research fields. Carbon dioxide is capable of activating desired changes in solvents and polymers, however, its application in wastewater treatment has not been conducted before. Based on this motivation, the main objective of the study was formed: designing CO_2-activated separation system for wastewater treatment.

The research background, motivation and objectives are followed by a detailed literature. The literature review discussed the four most common tertiary wastewater treatment techniques: membrane technologies, advanced photocatalytic oxidation, sand filtration and coagulation – flocculation. Each technique's advantages and disadvantages were discussed thoroughly. After the literature review on existing wastewater techniques, the history and the development of adsorption was introduced. This includes major events, breakthrough research and experiments since the beginning of the 19^{th} century. This was followed by a literature review on CO_2-activated systems, which introduces recent breakthrough research on CO_2-activated systems and the mechanism of CO_2 activation.

The final part of Chapter 1 discussed the main target pollutants of this study: dyes and pharmaceuticals. A structure of the dissertation was explained before moving on to Chapter 2.

Chapter 2: Carbon dioxide-activated system for removal of dyes

In Chapter 2, CO_2-activated separation system was applied for the adsorption of dyes on chitosan hydrogel. Compared with the conventional dye adsorption studies using chitosan hydrogel, this chapter emphasizes two major breakthrough results: improvement of chitosan's adsorption performance by CO_2 activation and enhancement of chitosan's stability by CO_2-activated cross-linking.

In the experimental section, the fabrication procedure of chitosan hydrogel, the adsorption procedure and the characterization experimental procedure were explained. Four different dyes were selected for adsorption on CO_2-activated chitosan: Brilliant Blue FCF (BBF), Congo Red (CR), Orange II (O-II) and Crystal Violet (CV). The differences of these dyes are in their chemical structures: BBF has three anionic groups on each molecule, O-II has one anionic group on each molecule, CR has two anionic groups and two cationic groups on each molecule and CV has one cationic group on each molecule. Amongst the four dyes tested, Brilliant Blue FCF and Orange II shows the highest removal efficiency due to having only anionic functional groups. Congo Red and Crystal Violet dyes have much lower removal efficiencies due to the presence of cationic groups, which cause electrostatic repulsion.

The CO_2-activated adsorption of BBF was investigated further to understand the effects of CO_2 on adsorption. It was found that carbon dioxide can activate amino groups on chitosan via protonation. The protonated amino groups, $-NH_3^+$, are capable of adsorbing anionic groups on dye molecules rapidly, such as sulfonic groups ($-SO_3^-$). The main adsorption mechanism is electrostatic attraction. The removal efficiency of BBF on CO_2-activated chitosan was also found to be significantly higher than chitosan in pure water within the range of initial concentrations up to 2000 mg L^{-1}. The time taken to reach adsorption equilibrium also increased with an increase of initial concentrations.

Furthermore, CO_2 was found to be capable of enhancing chitosan's stability at high temperatures. At 25°C in CO_2-activated separation system, chitosan dissolves due to the low stability of the protonated structure. However, when temperature was raised to 45°C, a carbamate cross-link was formed between chitosan and CO_2, which enhances chitosan's acid stability. Carbamate cross-link was confirmed by IR spectra of CO_2-activated chitosan, which shows a new peak at 1730 cm^{-1} of the C=O bond. The formation of cross-link between chitosan and CO_2 uses amino groups. The measurements of amino groups concentration by titration methods show that cross-linking by CO_2 reduce amino groups' concentration in the same way as a dilute cross-linking agent, sodium tripolyphosphate (TPP) 0.0082 M. This similarity was also confirmed by adsorption results: the BBF adsorption capacity of CO_2-activated chitosan and chitosan cross-linked by TPP 0.0082 M were found to be the same.

Chapter 3: Carbon dioxide-activated system for removal of pharmaceuticals

In this chapter, a hybrid CO_2-activated separation system was designed for the removal of a pharmaceutical compound, diclofenac (DCF), from aqueous solution. The hybrid system consists of two steps: CO_2-activated precipitation and CO_2-activated adsorption. In the first step, CO_2 was utilized to reduce the solubility of DCF in water. The introduction of CO_2 into the aqueous solution triggers the formation of neutral, insoluble DCF molecules from its original anionic form.

The effects of temperature, initial DCF concentration and CO_2 flow rate on the precipitation efficiencies are investigated. It was found that a lower temperature would lead to a higher precipitation efficiency in CO_2-activated separation system. Meanwhile, the rapid precipitation of DCF in CO_2-activated separation system could be achieved at the high DCF initial concentration and high CO_2 flow rate. After CO_2-activated precipitation, the concentration of DCF in the aqueous solution could be reduced to less than 5 mg L^{-1}.

In the second step, the remaining amount of DCF was removed by CO_2-activated adsorption. The target is to reduce DCF to a safe concentration for aquatic environment, which is less than 0.139 mg L^{-1} according to Jones et al. [1]. Three kinds of adsorbents with different surface charges were selected for DCF adsorption: chitosan, carbon nanotube (CNT) and carbon nanofiber (CNF). In CO_2-activated system, the –NH- group on DCF molecule is protonated to $-NH_2^+-$. Therefore, adsorption on chitosan was not effective due to the repulsion between the protonated amino group on DCF molecules and the protonated amino groups on chitosan molecules. Meanwhile, carbon-based adsorbents provided high adsorption efficiencies due to having a negative surface charge. This negative surface charge leads to the electrostatic attraction between the protonated structure of DCF and π-electron on the aromatic rings of the carbon-based absorbents. Carbon nanofiber in CO_2-activated system results in the adsorption efficiency of 97.6 % and the reduction of DCF concentration to less than 0.115 mg L^{-1}, which is within the safety limit reported by Jones et al [1]. Adsorption of DCF on carbon-based materials was also tested at various temperatures between 25 and 45°C. It was found that an increase in temperature would lead to a decrease in adsorption efficiency, which indicates an exothermic process.

Chapter 4: Adsorption modelling

In Chapter 4, the kinetics and isotherm models were evaluated for two adsorption processes: dye adsorption on CO_2-activated chitosan (Chapter 2) and CO_2-activated DCF adsorption on carbon materials (Chapter 3). In terms of kinetic models, pseudo-first-order and pseudo-second-order models were applied using non-linear regression method. In terms of isotherm models, Langmuir and Freundlich models were applied.

For the dye adsorption on CO_2-activated chitosan, it was found that dye adsorption on CO_2-activated chitosan follows pseudo-first-order model. This is because of the protonated structure of chitosan, which allows a direct access of dyes' anionic groups without surface chemical reaction. Furthermore, the first-order adsorption rate constant, k_1, was found to be higher in CO_2-activated separation system than that in pure water. This is the results of the effective and rapid electrostatic attraction between dye's anionic groups and chitosan's protonated amino groups. An interesting phenomenon was found when an increase in temperature of CO_2-activated adsorption leads to a decrease in adsorption rate constant. This unusual tendency is due to the effects of temperature on CO_2 dissolution: as temperature increases, less CO_2 dissolves into the aqueous solution, which leads to a slower adsorption rate constant. The dye chemical structure was found to affect strongly the adsorption kinetics: having a large number of charged chemical groups would lead to faster alignment onto adsorption sites. In terms of isotherm modelling, BBF adsorption in both pure water and CO_2-activated system was found to follow Langmuir model.

For adsorption of CO_2-activated DCF on carbon nanotube (CNT) and carbon nanofiber (CNF), it was found that adsorption on CNT follows pseudo-second-order model, while adsorption on CNF follows pseudo-first-order model. For adsorption of DCF on CNT, CO_2-activated separation system has a lower adsorption rate constant than pure water. For adsorption of DCF on CNF in CO_2-activated condition, there is a sudden jump of adsorption capacity, which reaches equilibrium at only 15 min. It was thought that this jump arises due to the combined contributions of large pore size, strong electrostatic attraction and π-π interaction between DCF molecules and CNF's carbon rings.

Chapter 5: Conclusion

Chapter 5 provides a summary of all research results and a future outlook for applying CO_2-activated separation system into industrial processes. In the outlook section, this chapter outlines several potential benefits of CO_2-activated separation system such as economic benefits and environmental benefits. It was also emphasized that the rapid adsorption behavior in CO_2-activated separation system is suitable for continuous, flow-type wastewater treatment processes.

References

[1] O.A.H. Jones, N. Voulvoulis, J.N. Lester, Aquatic environmental assessment of the top 25 English prescription pharmaceuticals, Water Res. 36 (2002) 5013–5022.