博 士（環境科学） 于 洪 文

学 位 論 文 題 名

Development of Novel Adsorbents for Environmental Remediation by Using Carbon Nanotubes as the Functional Sites

（カーボンナノチューブを素材にした吸着材料の開発と環境浄化応用）

学位論文内容の要旨

The elimination of chemical pollutants from a contaminated environment is one of the most important steps towards achieving the goal of environmental remediation. Dyes, such as the water-soluble organic dyes, typify a class of colored chemicals, being used extensively in textile, leather, paper, plastic and the other industries. Wastewaters discharged from these colorant industries often contain a certain amount of the water-soluble dyes, due to the inability to completely remove these highly water-soluble compounds by the common coagulation processes. The water-soluble organic dyes, especially the azo-type dyes, are suspected to be carcinogenic and are known to be potent acute and/or chronic effects on exposed organisms, depending on exposure time and the dye concentration. The water-soluble organic dyes are also capable of adsorbing/reflecting sunlight; this can have a strong detrimental effect on the growth of bacteria to levels sufficient to biologically degrade impurities. Moreover, the water-soluble organic dyes are highly visible to human eyes; this can cause aesthetic contamination even at very low concentrations. Elimination of the residual water-soluble organic dyes from the wastewaters is therefore an important activity to avoid the possible environmental contaminations by dyes.

In this study, carbon nanotubes (CNTs) was used for establishing adsorbents of high performance for elimination of the water-soluble organic dyes. This thesis paper composited of 5 chapters. In chapter 1, a brief introduction to CNTs as well as the difficulties encountered in elimination of water-soluble organic dyes is described.

In chapter 2, method for synthesizing sodium *n*-dodecyl itaconate, which is a polymerizable, anionic surfactant, has been used as the dispersant for dispersing agglomerates of CNTs into individuals, was described. CNTs, due to the high aspect ratio of each tube and the strong van der Waals attractions among the tubes, often occur as agglomerates of many of the individual tubes. Adsorption of chemical pollutants having higher molecular weights, such as the water-soluble organic dyes, is achieved mainly over the outmost surfaces of the CNT-based agglomerates. In other words, the tubes being involved in the innermost of the agglomerates often have no contributions to the adsorption of the chemicals of the large molecular weights. The dispersion method with using sodium *n*-dodecyl itaconate was capable of dispersing the agglomerates of CNTs into individual tubes; which in turn maximizing the overall adsorptive surfaces of CNTs.

In chapter 3, a micro-packing method followed by a permanent-immobilizing approach to

size-up the CNT-based adsorbent was described. The individuals of CNTs were inserted into the cavities of diatomaceous earth; this was then *in situ* immobilized by using polyurethane pre-polymer as binders. Macro-sized, durable, flexible and polyurethane foams (PUF) like type of adsorbent was established. Five typical water-soluble, organic dyes were used for studying the adsorptive capabilities of the CNT-based adsorbent. The advantageous properties of the resultant adsorbent were demonstrated by comparison with the data obtained using the agglomerates of the sole CNTs as adsorbents. Adsorption isotherms plotted based on Langmuir equation gave linear lines, suggesting the CNT-based adsorbent functioned in the Langmuir adsorption manner. The CNT-based adsorbents are durable, flexible and having large adsorbing surfaces. They are also reusable after regeneration using aqueous ethanol solution.

In chapter 4, a self-regeneration-able type of adsorbent was described. It was a CNT/ TiO_2 composite synthesized through a sol-gel method by using CNTs and titanium tetrabutoxide as the precursors. This CNT/TiO_2 composite functioned as an adsorbent but having photo-catalytic abilities. CNTs were demonstrated to be capable of enhancing the activity of the photo-degradation of aquatic humic substances.

In chapter 5, general conclusion and further prospect were drafted. CNTs are the cylindrically shaped graphite-like sp^2-bonded carbon entire materials. Their large specific surface areas, sharper curvatures together with their high thermal and chemical stabilities make them an idea application to the adsorption of pollutant chemicals, especially the water-soluble dyes having the aromatic backbones. These advantageous properties of CNTs were obtainable fully through the mono-dispersing, micro-packing and permanent-immobilizing strategies. Moreover, a self-regeneration-able type of adsorbent was obtainable by using CNTs in combination with photo-catalysts. All these achievements obtained in this study are highly beneficial to the field of environmental remediation.

学位論文審査の要旨

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Development of Novel Adsorbents for Environmental Remediation by Using Carbon Nanotubes as the Functional Sites

（カーボンナノチューブを素材にした吸着材料の開発と環境浄化応用）

In this study, the candidate has developed a new type of adsorbents for elimination of pollutant chemicals by using carbon nanotubes (CNTs) as the functional elements. The resultant achievements have been described in the thesis paper, which consisted of 5 chapters.

In chapter 1, a brief introduction to CNTs as well as the difficulties encountered in elimination of pollutant chemicals, especially for the water-soluble organic dyes, was described. Elimination of chemical pollutants from a contaminated environment is one of the most important steps towards achieving the goal of environmental remediation. Dyes typify a class of colored chemicals long used in textile, leather, paper, plastic, and the other industries. Wastewaters and/or effluents discharged from these industrial practices often contain a certain amount of dyes, especially water-soluble, organic dyes, because of the inability to completely remove the highly water-soluble dyes using common coagulation processes. Water-soluble organic dyes, especially compounds with aromatic backbones, are suspected carcinogens and known to exert potent acute and/or chronic effects on exposed organisms, depending on exposure time and dye concentration. The water-soluble organic dyes can also adsorb/reflect sunlight, which can inhibit the growth of bacteria to levels sufficient to biologically degrade impurities. Moreover, the human eye can easily detect water-soluble organic dyes, resulting in aesthetic contamination even at very low concentrations. Elimination of residual water-soluble organic dyes from wastewaters discharged from industrial colorants is therefore important to avoid possible environmental contaminations by dyes. The candidate, in this chapter, had critically understood the relevant literatures and the importance of the studies.

In chapter 2, a method for synthesizing sodium *n*-dodecyl itaconate, which is a polymerizable, anionic surfactant, has been used as the dispersant for dispersing agglomerates of CNTs into individuals, was described. CNTs, due to the high aspect ratio of each tube and the strong van der Waals attractions among the tubes, often occur as agglomerates of many of the individual tubes. Adsorption of chemical pollutants having higher molecular weights, such as the water-

soluble organic dyes, is achieved mainly over the outmost surfaces of the CNT-based agglomerates. In other words, the tubes being involved in the innermost of the agglomerates often have no contributions to the adsorption of the chemicals of the large molecular weights. The dispersion method with using sodium *n*-dodecyl itaconate was capable of dispersing the agglomerates of CNTs into individual tubes; which in turn maximizing the overall adsorptive surfaces of CNTs. This method, developed by the candidate, had a wide range of applications. The candidate, in this study, had made an original solution to the difficulties encountered in this field.

In chapter 3, a micro-packing method followed by a permanent-immobilizing approach to size-up the CNT-based adsorbent was described. The individuals of CNTs were inserted into the cavities of diatomaceous earth; this was then *in situ* immobilized by using polyurethane pre-polymer as binders. Macro-sized, durable, flexible and polyurethane foams (PUF) like type of adsorbent was established. Five typical water-soluble, organic dyes were used for studying the adsorptive capabilities of the CNT-based adsorbent. The advantageous properties of the resultant adsorbents were demonstrated by comparison with the data obtained using the agglomerates of the sole CNTs as adsorbents. Adsorption isotherms plotted based on Langmuir equation gave linear lines, suggesting the CNT-based adsorbent functioned in the Langmuir adsorption manner. The candidate has developed a new type of durable, flexible, CNT-based adsorbents, made an original contribution to both the fundament and application of this field.

In chapter 4, a self-regeneration-able type of adsorbent was described. It was a CNT/ TiO_2 composite synthesized through a sol-gel method by using CNTs and titanium tetrabutoxide as the precursors. This CNT/TiO_2 composite, developed by the candidate, functioned as an adsorbent but having photo-catalytic abilities. The candidate had demonstrated that the CNTs were capable of enhancing the activity for photo-degradation of aquatic humic substances; which giving new insights into the applicability of the CNTs.

In chapter 5, general conclusion and further prospect were drafted. CNTs are the cylindrically shaped graphite-like sp^2-bonded carbon entire materials. Their large specific surface areas, sharper curvatures together with their high thermal and chemical stabilities have made them an idea application to the adsorption of pollutant chemicals, especially the water-soluble dyes having the aromatic backbones. The candidate, in this study, has demonstrated that the advantageous properties of CNTs were obtainable through the mono-dispersing, micro-packing and permanent-immobilizing strategies. Moreover, the candidate has demonstrated that a self-regeneration-able type of adsorbent was obtainable by using CNTs in combination with photo-catalysts.

This thesis, as a whole, made an original contribution to the knowledge of this subject. The candidate had critically understood the relevant literatures. The methods adopted were appropriate to this subject. The experimental findings were suitably set out, also discussions were made scientifically. Qualities of English were satisfactory. The recommendation of all the examiners was that "the degree be awarded".