SYNTHESIS OF CARBON NANOTUBES ON IMPREGNATED POWDERED ACTIVATED CARBON FOR REMOVAL OF CADMIUM FROM WATER

BY

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ABSTRACT

Water resources are being polluted from various sources. Types of emerging pollutants are also increasing while the traditional pollutants are not solved efficiently yet. Removal of toxic metals is one of the biggest challenges in ensuring safe water for all. Those can be removed by chemical processes, physical processes such as ultra filtration and reverse osmosis, adsorption by polymers and various types of media which exhaust fast and expensive to reactivate. Cadmium (Cd^{2+}) was selected, in the present study, for its potential hazards to living beings at low concentration and difficulties in removing from water. Therefore, due to their high adsorption capacity and high surface area, carbon nanotubes (CNT) were synthesized and used to remove cadmium from water. Fixed catalyst chemical vapor deposition reactor (FCCVD) system was fabricated, upgraded and used to grow carbon nanotubes. Growth parameters (reaction time, reaction temperature, and gas flow rates) for CNT on powdered activated carbon (PAC), as a novel substrate were optimized. The PAC was impregnated with Fe^{3+} catalyst. Design Expert software was used to design the experimental plan and to determine the optimization parameters for the growth of CNT, considering removal (%) of Cd^{2+} as a response. Based on the screening test, four samples were selected for detailed study. Selected CNT-PAC samples were characterized using field emission electron microscope (FESEM) and transmission electron microscope (TEM) to confirm the CNT growth as well as to study the microstructure of the nanoscale product. In addition, the selected CNT-PAC samples were further characterized using Fourier transform spectroscopy (FTIR), thermal gravimetric analysis (TGA) and Brunauer, Emmett and Teller (BET) surface area. The surface properties of CNT-PAC were modified by oxidative functionalization using three different methods: sonication with $KMnO_4$, refluxing with HNO_3 at 140 ^oC and in-situ gasification with CO_2 at 750 ^oC. By comparing the performance, the best modified sample was found to be the one, which was functionalized with $KMnO_4$. Design Expert software was also used to optimize the removal of cadmium from water with pH, contact time, adsorbent dose and agitation speed as controlling parameters. $KMnO_4$ treatment of the most promising CNT-PAC sample (B3) enhanced the Cd^{+2} removal from 38.87% to 98.35%. Tip growth was observed from TEM. The results showed that BET surface area was 974.9 m^2/g, Zeta potential was - 46.1 mV and TGA combustion temperature range was between 371 ^oC and 560 ^oC. The selected functionalized sample was used to perform optimization study on removal of Cd^{2+} from water using central composite design (CCD) experimental design. The optimum conditions were pH 4.92, agitation speed 160 rpm, contact time 60 min and adsorbent dose 214 mg/L. Langmuir and Freundlich adsorption isotherms were studied for the novel adsorbent. Langmuir constants were q_m = 69.759 mg/g, K_l = 0.223 and R^2 = 0.924. The system was found more likely to follow Freundlich model with R^2 of 0.961, K_f of 9.215 and n of 3.015. Three kinetic models (pseudo first order, second order and intraparticle adsorption) of adsorption were studied too. The Pseudo-second-order was the best fit with R^2 of 0.996 and model constants were q_e = 34.29 (mg/g) and K_2 = 0.0013 (g/mg.min). Coefficients for the pseudo first order were q_e= 21.145 (mg/g) and K_1= 0.09 (min^{-1}) with R^2 of 0.936. The intraparticle kinetic model exhibited R^2 value of 0.812 with K_d = 1.295 (g/mg.$min^{0.5}$). The CNT-PAC adsorbent after oxidative functionalization with $KMnO_4$ was proven to be an efficient adsorbent for Cd^{2+} removal from water. Thus this novel nanocomposite material is promising for other adsorption applications for its significant surface properties.

خلاصة البحث

إن موارد المياه تتعرض لمصادر مختلفة من الملوثات. و أنواع الملوثات في زيادة و توسع وليست الطرق الشائعة للتنقية قادرة على ايجاد حلول نهائية لمشاكل التلوث. إن إزالة المعادن السامة من الماء تعد من التحديات الكبرى لتأمين المياه الصحية. عادة ما يتم ذلك باستخدام عمليات كيميائة أو فيزيائية مرتفعة الكلفة مثل الترشيح الفائق الدقة او الضغط الازموزي المنعكس أو البوليمرات بالإضافة إلى استخدام أنواع متعددة من المواد الممتزة و التي تستهلك بسرعة و يصعب أعادة تنشيطها و استخدامها لارتفاع الكلفة. تم اختيار معدن الكادميوم في هذة الدراسة لشدة خطورته على البشر و البيئة. ولذلك تم تحضير و تطوير مادةالانابيب النانو كاربونية لارتفاع قيمة مساحتها السطحية و سعتها الامتصاصية كي تستخدم لإزالة معدن الكادميوم من الماء. و لأجل ذلك تم تصنيع و تطوير منظومة مفاعل كيميائي تحليلي تبخيري ذو عامل مساعد ثابت كي تنمو فيه أنابيب الكربون النانوية (PAC-CNT). تمت دراسة (زمن التفاعل،و درجة حرارة التفاعل و نسبة خلط الغازات المستعملة الاسيتيلين إلى الهيدروجين) و هي ظروف و عوامل لنمو الانابيب النانوية الكربونية فوق سطح الفحم المنشط المسحوق كمادة جديدة. وهذا الكربون ا و الفحم المنشط قد حمل بأيونات الحديدالثلاثي التكافؤ Fe^{3+} ليتخذ عاملا مساعدا على التفاعل. وقد استخدم البرنامج الحاسوبي **Design Expert** لتصميم مخطط التجارب المختبرية للحصول على أفضل قيمة لكل واحدة من عوامل التفاعل على أن تتحقق في المنتوج أفضل كمية نمو مع أفضل قدرة على إزالة معدن الكادميوم. ومن خلال نتائج المسح الأولية تم اختار أربعة نماذج كي تدرس بالتفصيل. لقد فحصت خواص المادة الناتجة باستخدام FESEM و TEM لتأكيد نمو الأنابيب النانوية و دراسة التركيب السطحي الدقيق لها. اجريت فحوصات الأشعة تحت الحمراء ب FTIR و السلوك الحراري باستخدام TGA بالاضافة الى فحص المساحة السطحية بواسطة (BET). تم تحسين خواص سطح المنتج (CNT- PAC) بتفعيله بالأكسدة لتثبيت مجموعات كيميائية فعالة بثلاث طرق: المزج بالموجات فوق الصوتية مع ال $KMnO_4$ و التقليب في حامض النيتريك و الأكسدة بغاز ثاني اوكسيد الكربون بدرجة حرارة 750 مئوية. قورنت النماذج فكان أحسنها أداءا تلك التي عوملت بال$KMnO_4$. درست خواص المنتج النهائي فظهر أن النمو كان نموا طرفيا بالنسبة لأنابيب النانو من خلال الTEM. بينت النتائج الاخرى أن المساحة السطحية (BET) بلغت $974.9\ m^2/g$ و أن الجهد زيتا (Zeta potential) بلغ46.1 - mV و مدى الاحتراق كان ($371\ ^oC$) إلى ($560\ ^oC$). النموذج المختار و المفعل السطح استعمل في إزالة الCd^{2+} من الماء وقد كان التطور في القدرة على الازالة واضحا اذا ما قورنت النماذج المفعلة السطح بتلك التي لم يفعل سطحها قافزا من 38% إلى 98.35% أجريت عملية المفاضلة لاختيار أفضل الظروف لتفاعل الامتصاص وقد درست العوامل الآتية: pH و زمن التفاعل و جرعة المادة الممتزة و سرعة المزج فوجد أن أفضل القيم pH 4.92 والزمن 60 دقيقة و السرعة 160 دورة بالدقيقة و الجرعة 214 ملغرام باللتر. ولقد درست الأيزوثرم حسب (Langmuir) و (Freundlich) فكانت ثوابتها (R^2 0.924. q_m 69.759 mg/g, K_l 0.223) للأول و ($R^2 = 0.961, K_f =$ 9.215 and n =3.015) للثاني فكان هوخير ما يمثل النظام. ثم درست حركية التفاعل الامتزازي حسب ال(Pseudo first order) و ال (Pseudo-second-order) و ال (intraparticle) و كانت الثواب $R^2 = 0.996$ و q_e تساوي 34.29 (mg/g) و $K_2 = 0.0013$ (g/mg.min) و ذلك للنمط الثاني الذي مثل النظام خيرا من النمطين الاخرين. الذان كانت ثوابتهما كما يأتي: للنمط الأول (R^2=0.936) و(min^{-1}) K_1= 0.09 و q =21.145(mg/g) و ثوابت التداخل الجزيئي كانت R^2= 0.812 و ($g/mg.min^{0.5}$) K_d =1.295. ان المنتج (PAC-CNT) قد أبدى أداءًا متميزًا في الامتزاز مما جعل منه مادة واعدة في حال استخدامها لأغراض الامتزاز المتنوعة.

APPROVAL PAGE

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Mohammed A. Abdul Rahman

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATIONS AND SYMBOLS

AC	Activated Carbon
ANOVA	Analysis of Variance
BET	Brunauer–Emmet–Teller
CCD	Central Composite Design
CVD	Chemical Vapor Deposition
DE	Design Expert
DOE	Design of Expert
CNT	Carbon Nanotube
CNT-PAC	Carbon Nanotube Grown on Powdered Activated Carbon
FCCVD	Fixed Catalyst Chemical Vapor Deposition
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transforms Infrared
MWCNT	Multi Wall Carbon Nanotube
SWCNT	Single Wall Carbon Nanotube
PAC	Powdered Activated Carbon
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TGA	Thermo gravimetric analysis
C_0	Initial Concentration
C_t	Concentration at Time t
K_L	Langmuir Adsorption Constant
K_F	Freundlich Isotherm Constant
$1/n$	The Intensity Parameter in Freundlich Isotherm
K_1	Rate Constant of Pseudo-First-Order
K_2	Rate Constant of Pseudo-Second-Order Adsorption Kinetics
K_d	Rate Constant of Intraparticle Diffusion
m	Weight of Adsorbent
q_e	Equilibrium Adsorption Capacity
q_t	Adsorption Capacity at time t

q_m	Maximum Adsorption Capacity
R^2	Correlation Coefficient
V	Volume of Solution
Y	Yield

CHAPTER ONE

INTRODUCTION

1.1 OVERVIEW

Carbon nano materials (CNM) are being globally in the limelight as a new material in the 21st century and broadening their applications have been broadened in many areas, such as biotechnology, environmental energy, aerospace science, materials industry, medicine science, electronic computer, security and safety. CNM are known to be superior to many other existing materials in terms of strength, electrical properties, weight, size, etc. Carbon nanotubes (CNT) can be described as a rolled up one graphene sheet that is closed at each end with half of a fullerene denoted as single walled carbon nanotube, or more than one graphene cylinder nested one into another in case of multi walled carbon nanotubes - MWCNT (Delzeit et al., 2002; Dresselhaus et al., 2001; Stampfer et al., 2006). Among various types of CNM, carbon nanotubes (CNT) are in high demand especially in the following applications (Andrews et al., 2002; Popov, 2004; Tanaka et al., 1999).

a. Elevation of the existing electron emission current from 10 to 100 times level, using a low voltage;
b. High functional composites which can drastically enhance the strength of structures;
c. Various nanotechnologies; and
d. Bioenvironmental applications, such as pollutant removal, drug delivery, biosensors.

The potential benefits of the synthesis of nano-sized particles for remediation systems are the technology is portable, the nanoparticles are highly reactive and it can be scaled to contribute in resolving the pollution problems. Furthermore, it also has been found that carbon nanotubes can be used as an adsorbent for trapping volatile organic compounds (VOCs) and heavy metals from environmental samples (Feng et al., 2005). Many researchers as well as academic institutes dedicated great effort to it. CNT is a promising material especially in the field of remediation of toxic heavy metals contaminated industrial waste waters (Li et al., 2003; Liu et al., 2005; Lu & Chiu, 2006; Yantasee et al., 2007).

1.2 PROBLEM STATEMENT AND SIGNIFICANCE OF STUDY

Water resources are being polluted from various sources. Different types of emerging pollutants have been increasing while the removal of traditional pollutants is not solved efficiently yet. Cadmium is one of the most toxic metals, it is ranked the 6th of ten most toxic metals for its dangerous impacts on human health . Toxic metals (such as cadmium, lead, mercury, etc.) are becoming common in water. They are being removed by chemical processes or costly physical processes such as ultra filtration, reverse osmosis, polymers and various types of adsorbing media which exhaust very fast and costly to reactivate. Removal of toxic metals by adsorption is known technique. Adsorption is also related to the accessible surface area of the media. Therefore the CNT with high surface area could be potential to remove toxic metals for the production of high purity water.

Heavy metals are hazardous for the environment and human health as well. Due to high adsorption capacity, CNT are promising material to be applied in the environmental remediation to obtain water free from toxic metals (Atieh et al., 2005; Chen & Wang, 2006; Muataz et al., 2010). Many industrial and medical applications need ultra pure water for their products. Therefore, it is timely to conduct study on development of new materials to produce pure water for human consumption (Colt, 2006; Gil et al., 2006; Gomez et al., 2007; Koster et al., 2002).

In recent years, work has focused on developing Chemical Vapor Deposition (CVD) techniques using catalyst particles and hydrocarbon precursors to grow nanotubes; such techniques have been used earlier to produce hollow nanofibers of carbon in large quantities. CVD seems to be the most promising method for possible industrial scale-up due to the relatively low growth temperature, high yields and high purities that can be achieved (Cheol et al., 2002; Danafar et al., 2009; Dresselhaus et al., 2001; Kukovecz et al., 2005).

The catalyst substrate and floating catalytic chemical vapor deposition (FC-CVD) are very promising processes with respect to large-scale production of different kinds of carbon nanostructures materials as for example vapor growth carbon fibers, carbon nanofibers, multi, and single-walled carbon nanotubes. However, research is necessary to produce quantity of CNT at lower cost. There is also need to study the synthesis of CNT on low cost substrate for the immobilization process. Due to their attractive mechanical, thermal and electronic properties, researchers were more focusing on applications of CNT in other than water treatment fields where the cost plays major role (Zhong et al., 2007).

1.3 RESEARCH PHILOSOPHY

This research is an attempt to benefit from the CNT's physical and chemical properties in the field of environment (specifically water treatment), as one of the greatest challenges that facing the humanity in this century is the conservation of the water resources.

High surface area and presence of functional groups affect the adsorption properties of any adsorbent. Activated carbon (AC) is a well-known adsorbent for the removal of heavy metals despite its limited utility after the adsorption process. The synthesis of nanomaterial on PAC will therefore increase its surface functional groups and give longer span to its activity for the removal of heavy metals. The growth of carbon nanotubes (CNT) on the surface of powdered activated carbon (PAC) is thought to increase the adsorption capacity of the PAC and then the removal of cadmium from aqueous solutions.

1.4 RESEARCH OBJECTIVES

The objectives of this research are:

1. To design and fabricate a fixed catalyst chemical vapor deposition reactor (FCCVD) system for the production of CNT.
2. To optimize the growth of CNT on powdered activated carbon (PAC) by varying process parameters such as reaction time, reaction temperature, carrier gas flow rate and carbon source gas flow rate.
3. To optimize the removal of Cd^{2+} from water, with CNT on PAC dose, contact time, pH and initial concentration of pollutant as controlling parameters.
4. To investigate the isothermal adsorption behavior as well as the adsorption kinetics for the process of Cd^{2+} adsorptions in aqueous solution by impregnated CNT grown on PAC and determine the matching isotherm and kinetic models.