

**SURFACE MODIFICATION AND APPLICATIONS OF ELECTROSPUN
POLYACRYLONITRILE FIBER MATRICES**



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A Dissertation Submitted in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University
2012

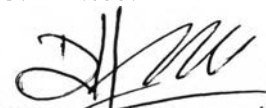
551761


Thesis Title: Surface Modification and Applications of Electrospun Polyacrylonitrile Fiber Matrices
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ABSTRACT

4982005063: Polymer Science Program
Pimolpun Kampalanonwat: Surface Modification and Applications
of Electrospun Polyacrylonitrile Fiber Matrices.
Thesis Advisors: Prof. Pitt Supaphol, 136 pp.
Keywords: Electrospinning/Chelating fibers/Metal ions removal/Stationary
phase/Ultrathin-layer Chromatography

Ultrafine polyacrylonitrile (PAN) fiber mats were prepared by electrospinning technique. Due to their important properties such as high surface area to volume ratio, high gas permeability and porosity, they were further modified their surface to improve their adsorption properties. To proof initial concept, the electrospun PAN nanofiber mat was treated with sodium hydroxide which is a simple reaction. This was achieved through the conversion of the nitrile functional groups on the surface of the PAN fibers into imine conjugated sequences. The chelating property of the hydrolyzed electrospun PAN fiber mats was evaluated against Cu(II) ions. For further improve adsorption properties of nanofibers adsorbent, the electrospun PAN was modified with diethylenetriamine (DETA) to contain amidino diethylenediamine groups on their surface via heterogeneous reaction. These nanofiber mats were investigated for the removal of silver, copper, iron, and lead ions in aqueous solution individually and under competitive adsorption condition. The effects of initial pH, contact time, initial ion concentration on adsorption of those ions were studied. In addition, one of the electrospinning highlight is its ability to produce binder-free plates and gives the scientist control of mat thicknesses and chemical functionality present using a minimal amount of materials. Therefore, electrospun PAN nanofiber mat also suitable to use as stationary phase for Ultra-thin layer chromatography. A manganese-activated zinc silicate was used as fluorescent indicator (UV₂₅₄) by mixing directly into polyacrylonitrile solution prior electrospinning process to visualize the UV-activated compounds.

บทคัดย่อ

พิมลพรรณ กำพลานนท์วัฒน์ : การปรับปรุงสภาพผิวและการประยุกต์ใช้แผ่นเส้นใยนาโนพอลิอะคริไลนไทรด์ที่ได้จากการขึ้นรูปโดยการปั่นเส้นใยด้วยไฟฟ้าสถิต (Surface Modification and Applications of Electrospun Polyacrylonitrile Fiber Matrices) อ. ที่ปรึกษา: ศาสตราจารย์ ดร. พิชญ์ ศุภผล 136 หน้า

แผ่นเส้นใยนาโนพอลิอะคริไลนไทรด์ที่ขึ้นรูปโดยใช้กระบวนการปั่นเส้นใยด้วยไฟฟ้าสถิต เนื่องจากคุณสมบัติที่สำคัญของเส้นใยนาโนได้แก่ พื้นที่ผิวต่อปริมาตรสูง ความสามารถในการผ่านของอากาศสูง และความเป็นรูพรุนสูง จึงได้มีการปรับปรุงพื้นผิวสัมผัสเพื่อให้มีคุณสมบัติในการดูดซับมากขึ้น ในงานวิจัยนี้ได้มีการศึกษาขั้นต้นโดยนำแผ่นเส้นใยพอลิอะคริไลนไทรด์มาทำปฏิกิริยาไฮโดรไลซิสกับโซเดียมไฮดรอกไซด์ ซึ่งสามารถทำได้ง่ายและรวดเร็ว ทำให้ได้แผ่นเส้นใยไฮโดรไลส์พอลิอะคริไลนไทรด์ หลังจากนั้นนำมาศึกษาคุณสมบัติการดูดซับโดยประเมินค่าจากพฤติกรรมดูดซับไอออนของทองแดง สามารถยืนยันได้ว่าการใช้เส้นใยที่มีขนาดเล็กกลงทำให้ความสามารถในการดูดซับมากขึ้น จากนั้นได้พัฒนาแผ่นเส้นใยโดยการเปลี่ยนหมู่ตรงที่ผิวเป็นกลุ่มเอมีนที่มีความสามารถในการใช้อิเลคตรอนร่วมกับไอออนของโลหะ โดยการนำแผ่นเส้นใยพอลิอะคริไลนไทรด์มาทำปฏิกิริยากับไดเอทิลีนไดเอมีนทำให้ได้หมู่อะมิโน ไดเอทิลีนไดเอมีนอยู่บนพื้นผิว จากนั้นนำแผ่นเส้นใยมาศึกษาคุณสมบัติในการจับโลหะ 4 ชนิด ได้แก่ ไอออนของเงิน ทองแดง เหล็ก และตะกั่ว ซึ่งศึกษาทั้งในสภาวะเดี่ยวและสภาวะผสม โดยศึกษาปัจจัยที่มีผลต่อการดูดซับ อาทิ เช่น ค่าความกรด-ด่างเริ่มต้น ระยะเวลาในการดูดซับ และความเข้มข้นเริ่มต้นก่อนการดูดซับ นอกจากนี้คุณสมบัติเด่นของแผ่นเส้นใยนาโนพอลิอะคริไลนไทรด์ที่สำคัญอีกประการหนึ่งคือ เมื่อปั่นเส้นใยลงบนแผ่นรองรับพบว่ามีเกาะตัวกับแผ่นรองรับได้ดีโดยไม่ต้องพึ่งสารเชื่อม และสามารถควบคุมความหนา นอกจากนี้ยังสามารถผลิตเส้นใยที่มีหมู่ฟังก์ชันที่ปรากฏบนผิวจำนวนมากโดยใช้สารละลายพอลิเมอร์ในปริมาณน้อย (~1 มิลลิลิตร) แผ่นเส้นใยอิเล็กโตรสปินจึงเหมาะกับการนำมาใช้เป็นเฟสอยู่กับที่โครมาโทกราฟีแบบชั้นบาง เมงกานีส ซิงค์ซัลไฟท์ ที่ได้รับการกระตุ้นถูกนำมาใช้เพื่อเป็นฟลูออเรสเซนอินดิเคเตอร์กระทำโดยการผสมโดยตรงในสารละลายพอลิเมอร์ก่อนกระบวนการปั่นเส้นใย ซึ่งหลังจากการแยกสารจะเห็นสารเป็นจุดสีดำบนพื้นสีเขียวสว่างของแผ่นโครมาโทกราฟีแบบชั้นบาง เมื่อทำการส่องด้วยแสงอัลตราไวโอเลตเฟสอยู่กับที่นี้ถูกนำมาศึกษาคุณสมบัติโดยใช้ในการแยกวัตถุกันเสีย 7 ชนิด และเปรียบเทียบกับแผ่นซิลิกาเจลที่ใช้เป็นเฟสอยู่ในปัจจุบัน

ACKNOWLEDGEMENTS

Appreciation is expressed to those who have made contributions to this dissertation. First the author gratefully acknowledges his advisors, Prof. Pitt Supaphol from The Petroleum and Petrochemical College, Chulalongkorn University, for giving her invaluable knowledge, meaningful guidance and encouragement all along the way. She also would like to express her sincere thanks to Professor Gertrud Morlock and from Institute of Nutritional Science, Justus-Liebig-University of Gießen for giving her useful advises, suggestions and opportunities to learn new research experiences and incredible ways of thinking while she did a short research at the Justus-Liebig-University of Gießen, Germany.

She gratefully acknowledges all faculty members and staffs at The Petroleum and Petrochemical College, Chulalongkorn University for their knowledge and assistance. Moreover she would like to give her special thanks to all members in her research group and all of her friends for their kind assistance, continual encouragement and wonderful friendship.

Asst. Prof. Pomthong Malakul, Prof. Pitt Supaphol, Prof. Anuvat Sirivat, Asst. Prof. Hathaikarn Manuspiya, and Dr. Orwan Suwantong are further acknowledged for being her dissertation committees, making valuable comments and suggestions.

She wishes to express her deep gratitude to his family for their unconditioned love, understanding and very supportive during all these years spent for her Ph.D. study.

Finally, she is grateful for the partial support received from the Petroleum and Petrochemical College; and the Center of Excellence for Petrochemicals and Materials Technology, Thailand and a doctoral scholarship received from the Royal Golden Jubilee PhD Program, The Thailand Research Fund (TRF) (PHD/0164/2550). This work would not be carried out successfully without all financial supports.

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ABBREVIATIONS

AAS	Atomic absorption spectroscopy
APAN	Aminated polyacrylonitrile
B	Benzoic acid
BE	Butyl 4-hydroxybenzoate
DETA	Diethylenetriamine
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EE	Ethyl 4-hydroxybenzoate
ePAN	Electrospun polyacrylonitrile
e-spun	Electrospun
FT-IR	Fourier-transform infrared spectroscopy
H-ePAN	Hydrolysed e-spun polyacrylonitrile
HPAN	Hydrolysed Polyacrylonitrile
HPLC	High pressure liquid chromatography
HPTLC	High performance thin-layer chromatography
IEC	Ion exchange capacity
ME	Methyl 4-hydroxybenzoate
PAN	Polyacrylonitrile
PE	Propyl 4-hydroxybenzoate
pHB	4-hydroxybenzoic acid
R _f	Retention factor
SEM	Scanning electron microscopy
So	Sorbic acid
TLC	Thin-layer chromatography
UTLC	Ultrathin-layer chromatography
UV	Ultra-violet
WHO	The world health organization
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

q	adsorption capacity
C_0	initial ion concentrations ($\text{mg}\cdot\text{L}^{-1}$)
C_e	equilibrium ion concentrations ($\text{mg}\cdot\text{L}^{-1}$)
V	volume of the testing solution (L)
M	initial, dry weight of the adsorbent
K_L	Langmuir adsorption equilibrium constant ($\text{mL}\cdot\text{mg}^{-1}$).
q_m	the maximal adsorption capacity of the metal ions on the adsorbent ($\text{mg}\cdot\text{g}^{-1}$)
K_F	Freundlich adsorption equilibrium constant [$\text{mg}^{(1-1/n)}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$]
k_1	the pseudo-first-order rate constant ($\text{mg g}^{-1} \text{min}^{-1}$)
k_2	the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).
r^2	the correlation coefficient
$D\%$	The desorption ratio (in %)
Z_s	The distance travelled by the analyte spot
Z_f	The distance travelled by the solvent front
N	Plate number
w	Spot width
R	The resolution
D_{R1}, D_{R2}	The retention distance of two adjacent peaks 1 and 2
w_1, w_2	The widths of two adjacent peaks 1 and 2,
κ	velocity constant
K_0	permeability constant of the layer
d_p	average particle size
ϕ	contact angle between the mobile phase and the layer
γ	surface tension of the mobile phase