REMOVAL OF ARSENIC AND CHROMIUM OXYANIONS BY HYDROUS TIN DIOXIDE AND TIN(IV)-LOADED EXCHANGERS

By

TAN WEE CHANG

Thesis Submitted to the school of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Master of Science

January 2005

DEDICATION

I Would like to dedicate this thesis to :

My Family Members,

My Supervisor,

My Co-supervisors,

My Friends,

All of those who were involved in this study…

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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The potential of tin-loaded poly(hydroxamic acid) ion exchange resin (SnPHA), hydrous tin dioxide ($SnO_2.xH_2O$) and hydrous tin dioxide-loaded poly(hydroxamic acid) resin (SnOPHA) to remove heavy metals As(V), As(III) and Cr(VI) from aqueous solution was investigated. Poly(hydroxamic acid) resin was prepared from poly methyl acrylate-divinyl benzene copolymer (PMA). The ester group of the PMA was converted to the hydroxamic acid using the hydroxylamine in an alkaline solution. The SnPHA was prepared by shaking the PHA resin with $SnCl_4$ solution. $SnO_2.xH_2O$ was prepared by neutralizing a Sn(IV) chloride solution with ammonia solution. The XRD result proved that the $SnO_2.xH_2O$ prepared is pure. The SnOPHA was produced by direct treating SnPHA with ammonia solution. The XRD result also contributed clear information about the oxidation stated of Sn(IV) in the PHA resin.

In order to understand the sorption characteristics of As(V), As(III) and Cr(VI) by the sorbents, batch and column studied were performed under various experimental conditions.

The parameters studied were pH, temperature, contact time, isotherm study, sorbent dosage, presence of competitive anions, flow rate and sorption-desorption cycles. The sorbents were also tested to remove arsenic and chromium from industrial waste water samples.

The results of batch study indicated that the sorption process by the sorbents was pH dependent and endothermic. It was found that the $SnO_2.xH_2O$ sorbent has the highest sorption capacity for As(V), As(III) and Cr(VI), followed by SnPHA and SnOPHA. Kinetic study showed that uptake of As(V) ion by the sorbents reached equilibrium after about 13 hours and about 10 hours for Cr(VI) sorption. The maximum sorption capacity of the SnPHA for As(V) and Cr(VI) at room temperature determined from the Langmuir isotherm were 38.50 mg-As/g-resin and 22.12 mg-Cr/g-resin, respectively. Meanwhile, the maximum sorption capacity of the SnOPHA were 8.30 mg-As/g-resin and 14.93 mg-Cr/g-resin and the maximum sorption capacity of the $SnO_2.xH_2O$ were 64.10 mg-As/g-sorbent and 28.57 mg-Cr/g-sorbent. The uptake increased with increasing sorbent dosage. In the presence of phosphate, sulphate and chromium anions, As(V) uptake decreased.

In desorption study, As(V) and Cr(VI) could be removed almost quantitatively from SnPHA and SnOPHA by eluting with a 0.2M NaOH solution. However, a rather low flow rates have to be applied for sorption using the column method. The SnPHA column could be used at least for 3 cycles and 2 cycles for SnOPHA for removal of As(V) ions. More than 86 % of arsenic and chromium were successfully removed from industrial waste water samples by SnPHA.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENYINGKIRAN ARSENIK DAN KROMIUM OLEH PENUKAR ION STANNUM DIOKSIDA TERHIDRAT DAN RESIN PENUKAR ION TERPEGUN STANNUM

Oleh

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Keupayaan resin penukar ion poli(asid hidroksamik)-terpegun Sn(IV) (SnPHA), tindioksida terhidrat ($SnO_2.xH_2O$), dan resin penukar ion poli(asid hidroksamik)-terpegun tindioksida terhidrat (SnOPHA) untuk penyingkiran logam berat As(V), As(III) dan Cr(VI) dari larutan akueus telah dikaji. Resin poli(asik hidroksamik) telah berjaya disediakan daripada kopolimer poli(metal akrilat)-divinil benzena (PMA). Kumpulan ester daripada PMA telah berjaya ditukarkan kepada asid hidroksamik melalui tindak balas dengan hydroksilamin hidroklorik dalam larutan alkali. SnPHA telah disediakan dengan menggongcang resin PHA didalam larutan $SnCl_4$. $SnO_2.xH_2O$ telah disediakan dengan meneutralkan Sn(IV) klorida dengan larutan ammonia. Ketulenan $SnO_2.xH_2O$ yang disediakan telah tentukan melalui analisis XRD. SnOPHA telah disediakan daripada SnPHA dengan tindakbalas secara langsung dengan larutan ammonia. Analisis XRD juga menunjukkan keadaan pengoksida Sn(IV) dalam resin PHA.

Untuk memahami ciri-ciri erapan SnPHA, $SnO_2.xH_2O$ dan SnOPHA terhadap As(V), As(III) dan Cr(VI), kajian kelompok dan turus telah dijalankan di bawah pelbagai keadaan eksperiment seperti pH, suhu, masa, isoterma,dos pengerap, kehadiran ion-ion saingan, kadar aliran, erapan-penyaherapan dan rawatan terhadap sampel air buangan industri.

Keputusan kajian kelompok menunjukkan bahawa proses erapan dipengaruhi oleh pH dan bersifat endotermik. Didapati $SnO_2.xH_2O$ menunjukkan keupayaan erapan yang paling tinggi bagi As(V), As(III) dan Cr(VI) dan diikuti dengan SnPHA dan SnOPHA. Kajian kinetik menunjukkan keseimbangan tindakbalas bagi erapan As(V) dan Cr(VI) masing-masing diperolehi selepas 13 jam dan 10 jam. Kapasiti erapan maksimum untuk SnPHA pada suhu bilik yang ditentukan daripada isoterma Langmuir adalah 38.50 mg-As/g-pengerap dan 22.12 mg-Cr/g-pengerap. Manakala kapasiti erapan maksimum untuk SnOPHA adalah 8.30 mg-As/g-pengerap serta kapasiti erapan maksimum untuk $SnO_2.xH_2O$ adalah 64.10 mg-As/g-pengerap dan 28.57 mg-Cr/g-pengerap. Erapan meningkat dengan peningkatan dos pengerap. Kehadiran ion-ion saingan akan mengurangkan erapan ion logam.

Dalam kajian penyaherapan, hampir semua As(V) dan Cr(VI) dapat disingkirkan dari SnPHA dan SnOPHA dengan larutan 0.2 M NaOH. Walau bagaimana pun, untuk pengerapan yang berkesan, kadar aliran yang perlahan harus digunakan. Turus SnPHA dapat digunakan secara berkesan tidak lebih daripada 3 kali manakala turus SnOPHA dapat digunakan tidak lebih 2 kali. Lebih 86 % daripada logam As(V) dan Cr(VI) dalam sampel air buangan industri dapat disingkirkan oleh SnPHA.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere appreciation and gratitude to my supervisor, Assoc. Prof. Dr. Md. Jelas Haron and co-supervisors, Prof. Dr. Wan Md. Zin Wan Yunus and Prof. Dr. Anuar Kassim for their supervision, invaluable guidance, unfailing help, advice and suggestion throughout the duration of this study. We thank Ministry of Science and Technology and Environment for financial support through the Intensification of Research in Priority Areas, IRPA funds.

I would like to take this opportunity to extend my deepest appreciation to all the staff in Chemistry Department, especially to Madam Choo and Mr. Kamal for their assistance and cooperation that in one way or another has contributed to the success of this study.

My sincere gratitude is also extended to my course mates and friends for their help, encouragement and comments which have contributed towards the success of this study.

Last but not least, I would like to express my deepest affection to my beloved family for their caring, patience, support and understanding.

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master. The members of the Supervisory Committee are as fullows:

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DECLARATION

I hereby declare that this thesis is based on my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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TABLES OF CONTENTS

	Page
DEDICATION	II
ABSTRACT	IV
ABSTRAK	V
ACKNOWLEDGEMENTS	VIII
DECLARATION	X
LIST OF TABLES	XIV
LIST OF FIGURES	XV
LIST OF SYMBOLS AND ABBREVIATIONS	XVIII
CHAPTER	
I INTRODUCTION	1
OBJECTIVES OF STUDY	5
II LITERATURE REVIEW	
Arsenic	6
Chromium	10
Stannum/Tin	16
Ion Exchanger	17
Cation exchanger	19
Anion exchanger	19
Chelating ion exchanger	20
Efficiency In Heavy Metal Removal	24
Ligang Exchanger	26
Inorganic Ion Exchanger	29
Hydrous tin dioxide	30
Parameter Study	
Kinetic of ion exchange reaction	32
Sorption isotherm at different concentrations	33
Competitive of other ions	33
Column study	34
Treatment of Heavy Metals	35
III MATERIALS AND METHODS	
Reagents	45
Industrial Wastewater	45
Instrumental Analysis	46
Material Preparation and Characterization	49
Preparation of starting polymer (PMA)	49
Converting PMA to PHA	49
Loading tin metal ion to PHA resin	50

Preparation of hydrous tin dioxide 50
Preparation and reloading of SnO_2PHA resin 51
Characterization of sorbents 51

Batch Experiments 53
Effect of pH 54
Effect of contact time 54
Sorption isotherm 54
Effect of temperatures 54
Effect of sorbent dosage 55
Effect of competitive ions 55
Desorption study 55
Column Study 56
Effect of flow rate 56
Sorption-desorption cycles 56
Separation of As(III) and As(V) 57
Treatment of Industrial Wastewater 57
Removal of heavy metals from industrial wastewater 57

IV RESULTS AND DISCUSSION
Preparation of Poly(hydroxamix acid) Resin 58
Synthesis of PMA 58
Converting PMA to PHA 58
FTIR Spectrum of PMA and PHA resins 60
Loading Tin Metal Ion to PHA Resin 62
Preparation of Hydrous Tin Dioxide 63
Preparation of SnOPHA Resin 64
X-ray spectra for $SnO_2.xH_2O$ and SnOPHA 66
Surface Charge Study 67
Batch Experiments
Sorption of As(V) by unloaded PHA resin at various pH 70
Sorption of metal ions by SnPHA resin at various pH 71
Sorption of metal ions by $SnO_2 .xH_2O$ at various pH 75
Sorption of metal ions by SnOPHA at various pH 77
Sorption kinetic 81
Sorption isotherm 89
Effect of temperature 97
Effect of sorbent dosage 102
Effect of competitive ions 107
Desorption study 111
Column Study
Effect of flow rate 112
Sorption-desorption study 114
Treatment of Industrial Wastewater 117
Removal of metal ions from wastewater by SnPHA resin 117

Removal of metal ions from wastewater by SnOPHA resin 118
Separation of As(V) and As(III) 118

V CONCLUSIONS 121

REFERENCES / BIBLIOGRAPHY 123
APPENDIXS 132
BIODATA OF THE AUTHOR 146