

PREPARATION AND CHARACTERIZATION OF RADIATION GRAFTED
FIBROUS ADSORBENT CONTAINING N-METHYL-D-GLUCAMINE FOR
BORON REMOVAL

TING TEO MING

UNIVERSITI TEKNOLOGI MALAYSIA

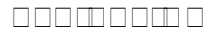
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FIBROUS ADSORBENT CONTAINING N-METHYL-D-GLUCAMINE FOR
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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

JUNE 2015



To my parents, my wife and my children for their supports and understandings

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First and foremost, I would like to express my gratitude to my supervisor Professor Dr. Mohamed Mahmoud El-Sayed Nasef for his guidance, advices, motivation and commitment throughout this study. He has given me a tremendous effort with constant encouragement in the preparation and completion of this study. I would also like to thank my co-supervisor, Dr. Kamaruddin Hashim for his advices, inputs and infinitive support to this study.

The experiments were conducted in the laboratories and facilities provided by Radiation Processing Technology Division and Irradiation Services Division of Malaysian Nuclear Agency. Therefore, I wish to thank the staff in both divisions for their help and support. My appreciation also goes to my friends and colleagues for their valuable suggestion and assistance.

This study was funded by the Ministry of Science, Technology and Innovation (MOSTI) through E-Science Fund, Malaysian Nuclear Agency and JPA. I am grateful to them and this make the implementation of this study could be carried out successfully.

Finally, I would like to share the accomplishment of this research with my parents, wife and children. Their support and encouragement have contributed significantly towards the completion of this study.



Water contamination with boron is currently increasing due to its multiple uses in various chemical industries and this poses threats to the environment and human health. Removal of boron by ion exchange resin is the most suitable technology but it is challenged by high cost of resins and slow kinetics. To overcome this problem, a new fibrous adsorbent containing glucamine for removal of boron from solutions was prepared by radiation induced graft copolymerization (RIGC) of vinylbenzyl chloride (VBC) onto nylon-6 fibers followed by functionalisation with N-methyl-D-glucamine (NMDG). The best combination of grafting parameters required for achieving the highest degree of grafting (DG) was determined. The density of glucamine loaded in the adsorbent was tuned by optimisation of the reaction parameters using response surface methodology (RSM) employing Box–Behnken design (BBD). The obtained adsorbent was characterized using various materials and analytical research techniques (scanning electron microscopy (SEM), Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and mechanical tester) to confirm the incorporation of poly(VBC) and glucamine groups and to evaluate the impact of preparation procedure on the adsorbent's physico-mechanical properties. The performance of the fibrous adsorbent under various conditions pertaining to equilibrium isotherms, kinetics and thermodynamics of boron adsorption from aqueous solutions were evaluated using relevant models. The DG was found to be a function of reaction parameters and could be tuned to 130% at 20 wt% VBC concentration in methanol, 300 kGy absorbed dose, 30 °C and 3 h. The optimum parameters for achieving a glucamine density of 1.7 mmol/g in the adsorbent are 10.6%, 81 °C, 47 min and 121% for NMDG concentration, reaction temperature, reaction time and DG, respectively. The deviation between the optimum experimental and predicted glucamine density is found to be 1.2% suggesting the reliability of RSM in predicting the yield and optimising the functionalisation reaction parameters. The boron adsorption equilibrium followed Redlich-Peterson isotherm. Moreover, the adsorption is governed by a film diffusion mechanism and occurs spontaneously. The results of this study suggest that a new fibrous adsorbent having a higher adsorption capacity and faster kinetics than commercial granular resin is obtained and has the potential application in boron removal from aqueous solutions.



Pencemaran air dengan boron pada masa ini semakin meningkat kerana pelbagai kegunaan dalam pelbagai industri kimia dan ini menimbulkan ancaman kepada alam sekitar dan kesihatan manusia. Penyingkiran boron dengan resin pertukaran ion adalah teknologi yang paling sesuai tetapi ia dicabar oleh kos resin yang tinggi dan kinetik yang perlahan. Untuk mengatasi masalah ini, penjerap gentian baru yang mengandungi glukamina untuk penyingkiran boron dari larutan telah dihasilkan dengan kaedah pengkopolimeran cangkuk aruhan sinaran. Vinil benzil klorida (VBC) dicangkukkan ke atas gentian nilon-6 dan diikuti pengfungsian dengan N-metil-D-glukamina (NMDG). Kombinasi parameter terbaik cangkukan diperlukan untuk mencapai kadar cangkukan (DG) yang tertinggi telah ditentukan. Ketumpatan glukamina dimuatkan ke atas gentian cangkukan ditalakan dengan mengoptimumkan parameter reaksi menggunakan kaedah gerak balas permukaan (RSM) reka bentuk *Box-Behnken* (BBD). Penjerap gentian yang diperoleh dicirikan dengan menggunakan pelbagai bahan dan teknik penyelidikan analisis (mikroskop pengimbasan elektron (SEM), spektrometer transformasi *Fourier* inframerah (FT-IR), spektrometer pembelauan sinar-X (XRD), kalorimetri pengimbasan pembezaan (DSC), analisis termogravimetri (TGA) dan penguji mekanikal) untuk mengesahkan pembentukan poli(VBC) dan kumpulan glukamina serta menilai impak prosedur penyediaan ke atas sifat fiziko-mekanikal penjerap. Prestasi penjerap gentian di bawah pelbagai keadaan berhubung dengan keseimbangan isoterma, kinetik dan termodinamik penyerapan boron dari larutan akueus telah dinilai dengan menggunakan model berkaitan. Kadar cangkukan didapati berfungsi dengan parameter reaksi dan boleh ditala kepada 130% pada kepekatan VBC 20% dalam metanol, 300 kGy dos terserap, 30 °C dan 3 jam. Parameter-parameter yang optimum untuk mencapai ketumpatan glukamina 1.7 mmol/g dalam penjerap adalah masing-masing 10.6%, 81 °C, 47 minit dan 121% untuk kepekatan NMDG, suhu tindak balas, masa tindak balas dan DG. Sisihan ketumpatan glukamina antara eksperimen optimum dan ramalan didapati 1.2% mencadangkan kebolehpercayaan RSM dalam meramal hasil dan mengoptimumkan parameter reaksi pengfungsian NMDG. Keseimbangan penjerapan boron adalah mengikut isoterma *Redlich-Peterson*. Selain itu, penjerapan boron dikawal oleh mekanisma lapisan difusi dan boleh berlaku secara spontan. Hasil kajian ini mencadangkan bahawa penjerap gentian terbaru mempunyai kapasiti penjerapan yang lebih tinggi dan kinetik lebih cepat berbanding resin butiran komersial, diperoleh dan berpotensi untuk diaplikasikan dalam penyingkiran boron daripada larutan akueus.

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ATR	-	Attenuated total reflectance
ATRP	-	Atom transfer radical polymerization
BBD	-	Box–Behnken design
Co-60	-	Cobalt-60
CV	-	Coefficient of Variance
DG	-	Degree of grafting
DMF	-	Dimethylformamide
DMSO	-	Dimethyl sulfoxide
DOE	-	Department of Environment
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermogravimetry
DVB	-	Divinylbenzene
EB	-	Electron beam accelerator
EU	-	European Union
FT-IR	-	Fourier transform infrared spectrometer
GMA	-	Glycidyl methacrylate
GPTMS	-	3-Glycidoxypropyl trimethoxysilane
ICP-OES	-	Inductively coupled plasma optical emission spectrometry
NMDG	-	N-methyl-D-glucamine
PE	-	Polyethylene
PP	-	Polypropylene
RAFT	-	Reversible addition fragmentation chain transfer
RIGC	-	Radiation induced graft copolymerization
RSM	-	Response surface method
SEM	-	Scanning electron microscopy
SV	-	Space velocity

TGA	-	Thermogravimetric analysis
VBC	-	Vinylbenzyl chloride
WHO	-	World Health Organization
XRD	-	X-ray diffraction

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a	-	Initial rate of sorption (mg min/g)
A_R	-	Redlich–Peterson isotherm constant (1/mg)
b	-	Level of surface coverage and activation energy of chemisorptions (g/mg)
C	-	Thickness of the boundary layer (mg/g)
C_e	-	Concentration of boron in the solution at equilibrium (mg/L)
C_f	-	Final concentration of boron in the solution (mg/L)
C_o	-	Initial concentration of boron in the solution (mg/L)
g	-	Redlich–Peterson isotherm exponent
ΔG^o	-	Gibb’s free energy change (kJ/mol)
h	-	Initial adsorption rate (mg/g min)
ΔH_f	-	Heat of fusion (J/g)
ΔH^o	-	Enthalpy change (kJ/mol)
k_1	-	Rate constant of the pseudo-first order sorption (1/min)
k_2	-	Pseudo second order rate constant of sorption (g/mg min)
K_D	-	Equilibrium constant
K_F	-	Freundlich adsorption constant (mg/g) (L/mg) ^{1/n}
k_{ip}	-	Rate constant for intra-particle diffusion (mg/g min ^{0.5})
K_L	-	Langmuir adsorption constants related to adsorption energy (L/g)
K_R	-	Redlich–Peterson isotherm constants (L/g)
M	-	Molecular weight (g/mol)
q_{cal}	-	Calculated adsorption capacity (mg/g)
q_e	-	Boron adsorption capacity at equilibrium (mg/g)
q_{exp}	-	Experimental adsorption capacity (mg/g)

Q_L	-	Langmuir adsorption constants related to adsorption capacity (mg/g)
q_{ref}	-	Solid phase concentration at time $t = t_{ref}$ (mg/g)
q_t	-	Amount of boron adsorbed at t time (mg/g)
Δq	-	Normalized standard deviation (%)
r^2	-	Correlation coefficients
R	-	Gas constant (8.314 J/mol K)
R_i	-	Initial adsorption factor of the intra-particle diffusion model
ΔS^o	-	Entropy change (J/mol K)
t	-	Time (min)
T	-	Temperature (K)
T_m	-	Melting temperature ($^{\circ}$ C)
t_{ref}	-	Longest time in the adsorption process (min)
V	-	Volume of the solution (L)
W	-	Weight (g)
W_f	-	Final weight (g)
W_i	-	Initial weight (g)

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Boron is widely distributed in the lithosphere and hydrosphere in a relatively low concentration depending on the geological composition and geographical location [1,2]. In nature, boron does not exist in an elemental state and elemental boron also does not have any commercial importance. Particularly, boron is always found bound to oxygen and other elements to form boric acid or borates (inorganic salts) that have commercial importance. Almost 90% of boron consumption by industry worldwide comprise of four borates minerals namely, colemanite, kernite, tincal and ulecite [3].

Boron is very soluble and mobilised by natural weathering reactions of rocks and soils containing borate minerals. Therefore, the natural occurring of boron and its concentration found in various water bodies depend on location. For example, boron concentration as high as 7 mg/L in surface water bodies has been reported in Russian and Turkey as compared to average boron concentration of 0.5 mg/L in other places. Boron concentration in the Mediterranean Sea can reach 9.6 mg/L as compared to average boron concentration in seawater at 4-5 mg/L [4,5].

Complete removal of boron from food chains will result in boron deficiency and a slightly higher consumption of boron leads to toxicity in the living organisms. The range of boron deficiency and toxicity to the plants are very narrow [6,7]. For

example, irrigation waters with 0.5 mg/L boron can promote growth of plants, while concentration at 1 mg/L causes toxicity and productivity of crop to reduce [8,9].

Boron is needed as micronutrients for human and animals. It is also required for various metabolisms of macro nutrients in the organs. For example, the deficiency of boron can cause reduction in the adsorption of calcium and magnesium [10]. On the other hand, the consumption of boron at high concentration can lead to toxicity and damage to the organs [11,12]. Due to the adverse impact of boron to living organisms, it is necessary to reduce the concentration of boron in waters.

Currently, research on boron removal from wastewater is receiving an increasing attention to meeting the wastewater discharge standards set by environmental authorities in various countries. Different techniques have been utilized to treat a variety of streams with different boron contents. Conventional methods do not significantly remove boron. Only ion exchange technology is found to be the most effective and efficient method to remove boron from waters and wastewaters to low desired levels [13-21]. Boron selective resins is the heart of ion exchange process where boron adsorption takes place in a column that provides a continuous mode of operation or otherwise resins are used on a batch basis in continuous stirred tanks [22]. The batch adsorption study is used to study the interaction of adsorbate and adsorbent. The data obtained is used to establish the adsorption isotherm, kinetics, and thermodynamics of boron adsorption.

The performance limitations of commercial resins have triggered a research interest for developing new alternative adsorbents with improved performance marked by high adsorption capacity and fast adsorption kinetics. Considering the physical form of the adsorbent/resins, adsorption of heavy metal ions on adsorbents having fibrous structure was found to be more efficient than granular resins [23].

Radiation induced graft copolymerization (RIGC) is an effective polymer modification technique that has received the most interest for developing adsorbents for removal or recovery of metals from solutions [24]. This is because its versatility in allowing polymeric materials of any forms (fiber, fabric and membrane) to be modified with variety of function groups in large quantities [25]. Thus, substrate

polymer with strong physical and mechanical properties can be selected to prepare adsorbents with desired ionic groups. Moreover, the use of RIGC in preparation of adsorbents allows tuning the content of the functional groups through a facile chemical route.

In principle, the RIGC is a reaction that starts by exposing a polymer substrate to high-energy radiation such as γ -rays (from Co-60) and accelerated electrons (from electron beam accelerator (EB)) which leads to formation of radicals (active sites). The reaction is initiated when monomer molecules are introduced leading to formation of macroradicals, which propagate forming graft growing chains [26]. There are three methods for RIGC to proceed with: pre-irradiation, simultaneous and peroxidation methods. In pre-irradiation method, polymer substrate is irradiated under vacuum or inert condition to produce free radicals, which is trapped by freezing. The reaction proceeds on the irradiated polymer by adding a monomer at an elevated temperature. In simultaneous method, the polymer is irradiated together with the monomer leading to formation of free radicals on both of them and the copolymerization reaction proceeds in a competition with homopolymerization. Peroxidation method is similar to the pre-irradiation under inert atmosphere but it differs in the irradiation step, which is normally carried in the presence of air or oxygen.

The yield of grafting or the amount of monomer grafted onto the polymer backbone is controlled by the reaction parameters such as irradiation dose, monomer concentration, type of solvents, reaction temperature and time [26,27]. The degree of grafting (DG) required to prepare a good adsorbent is ranged between 100–200 % and this can be obtained by optimisation of the grafting reaction parameters [28]. If the grafted monomer does not have function group, it forms an adsorbent precursor, which can be chemically modified in a post grafting reaction to impart ionic moiety. The selection of the functional group depends on the target ionic pollutants to be removed. For example, the N-methyl-D-glucamine (NMDG) functional group is selected for making boron-selective resins and adsorbents because of its strong affinity towards boron ions in solutions [21,29].

The polymers used as substrate for RIGC can be divided into two categories. First, synthetic polymers such as polyethylene (PE), polypropylene (PP) and nylon are selected as substrates for various adsorbents due to their cheap cost, abundance mechanical integrity and good reactivity in the grafting system [21,30]. Secondly, natural polymers such as starch and chitosan have weak chemical and thermal properties and therefore, they are less likely to be used for making adsorbents as their structural backbone degrade and become unstable when exposed to radiation during preparation and harsh chemical environment during application.

Among synthetic polymers nylon-6 fibers have excellent characteristics of textural properties, mechanical strength, chemical and thermal stability [21,31]. Despite the exposure of nylon-6 fibers to a high irradiation dose and reaction with various solvents during preparation procedure, they retain a great deal of their physical and mechanical properties, which make them favorable for development of adsorbents for water treatment and other environmental application.

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Boron is consumed by many industries and these activities contribute to the increase in the concentration and complexity of boron found in surface water or wastewater. In Malaysia, wastewater generated from ceramic industry contains a high concentration of boron. Leachate from the integrated scheduled waste treatment facility operated by Kualiti Alam Sdn Bhd also contains a high boron concentration of up to 100 ppm. Due to the adverse health impact of boron to the living things, the contamination of boron found in wastewater needs to be removed and controlled to comply with the legislation requirement by Malaysian Department of Environment (DOE) with the limit of 1 and 4 mg/L for effluent discharge standards A and B, respectively (Environmental Quality Act, 1974).

Currently, commercial resins show high selectivity towards boron. However, they have relatively low adsorption capacity and slow adsorption kinetics both of which have adversely affected the performance of boron removal system and its

economy. In addition, the loss of capacity upon scaling up and after each regeneration cycle, the limited surface areas, uncontrollable pore structures and hydrophobicity characteristic of the resins have resulted in unsatisfactory performance of the commercial resins. Therefore, development of new, highly boron selective adsorbents, with high adsorption capacity and fast adsorption kinetics is highly needed to effectively enhance the performance of the ion exchange process for boron removal and eliminate the problems associated with commercial granular resins.

Selective adsorbents having fibrous structure have been found to be more efficient in ions removal compared to granular resins. Fibrous adsorbents with a diameter of 50 μm and below could be obtained compared to commercial granular resins, which have particle diameters of above 300 μm . This gives faster adsorption kinetic and higher boron uptake capacity upon using fibrous adsorbents. The fibrous structure also could reduce the loss of applied pressure when the adsorbent is applied in a column under high flow rate and pressure.

RIGC using electron beam irradiation provides an effective and convenient method to graft monomer onto polymer substrates and subsequent NMDG functionalisation to produce fibrous chelating adsorbent. Therefore the prepared adsorbent using RIGC technique and subsequent functionalisation is expected to offer better alternative for boron removal from solutions.

Radiation grafting of glycidyl methacrylate (GMA) onto polyethylene coated polypropylene (PE-PP) non-woven fabric and grafting of GMA onto nylon fiber were reported for preparation of fibrous boron-selective adsorbents. However, the obtained adsorbents are fragile and lack of chemical stability especially when the degree of grafting is higher than 100%. The former is caused by the highly amorphous nature of the incorporated poly(GMA) whereas the latter takes place during the adsorbent regeneration process.

To improve the stability of fibrous adsorbents, grafting of vinylbenzyl chloride (VBC), a monomer that has higher chemical stability than aliphatic GMA because of its aromatic structure, offers an alternative that can confer fibrous

substrates phenyl groups which can be easily activated with the boron selective group using a mild reaction. Moreover, VBC has neither been grafted on nylon-6 fiber nor used for preparation of fibrous adsorbent for boron removal.

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The main objective of this study is to prepare, characterize and test a new fibrous boron selective adsorbent for removal of boron from solutions using radiation induced grafting and subsequent functionalisation with NMDG. The objective can be divided into sub-objectives as follows:

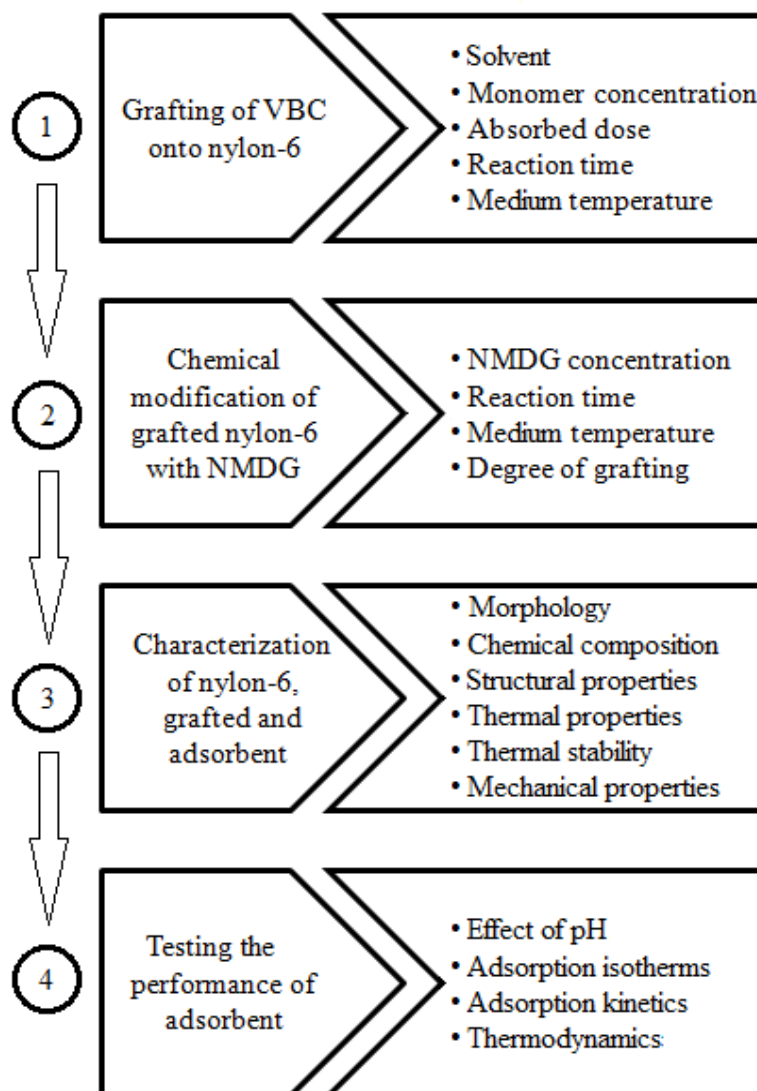
- i. To investigate the effects of reaction parameters on the degree of VBC grafted onto nylon-6 fibers.
- ii. To optimize the reaction parameters with respect to the density of NMDG groups incorporated in the poly(VBC) grafted nylon-6 fibers.
- iii. To evaluate the properties of the obtained adsorbent and its corresponding precursor using chemical and material research techniques.
- iv. To assess the performance of the prepared adsorbent in a batch reactor system and establish the relationship between the operating parameters and the boron removal capacity.
- v. To establish equilibrium isotherms, kinetics and thermodynamic behaviors of boron adsorption onto the newly prepared fibrous adsorbent in comparison with commercial resin.



New boron-selective adsorbent is prepared using RIGC technique in 3-stages i.e. irradiation, grafting and subsequent treatment with NMDG as depicted in Figure 1.1. The scope of work can be outlined as follows:

- i. Preparation of adsorbent precursor by RIGC of VBC onto nylon-6 under various grafting parameters including:
 - Type of solvents, which included using methanol, ethanol, propanol, butanol and pentanol as a diluents.
 - Monomer concentration, which was varied in the range of 1–100%.
 - Absorbed dose, which was varied in the range of 25–500 kGy.
 - Reaction temperature, which was varied in the range of 5–70 °C.
 - Reaction time, which was varied from 30 minutes to 48 hours.
- ii. The poly(VBC) grafted nylon-6 fibers were chemically modified using NMDG solution in 1-4 dioxane to impart the ionic character to the grafted fibers under different reaction parameters.
- iii. The chemical modification parameters that were investigated included:
 - Concentration of NMDG, which was varied in the range of 5–15%.
 - The DG in the precursor was chosen in the range of 70–130%.
 - Reaction time, which was varied in the range of 10–60 minutes.
 - Reaction temperature, which was varied in the range of 70–90 °C.
- iv. Determination of the physical and chemical properties of the newly prepared adsorbent with reference to the original and poly(VBC) grafted nylon-6 fibers. The investigated properties included:
 - Morphology, which was observed using scanning electron microscopy (SEM).
 - Chemical composition, which was investigated using Fourier transform infrared spectrometer (FT-IR).

- Structural properties, which was evaluated using X-ray diffraction (XRD).
- Thermal properties, which was measured using differential scanning calorimetry (DSC).
- Thermal stability, which was tested using thermogravimetric analysis (TGA).
- Mechanical properties, which was measured using a universal mechanical tester.



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- v. The performances of the prepared adsorbent with reference to the commercial resin, Diaion CRB 03 were tested under same adsorption conditions. The reaction parameters that were investigated included:
 - Initial boron concentration, which was varied in the range of 20–500 mg/L.
 - Reaction temperature, which was varied from 20–40 °C.
 - pH, which was varied in the range of 2–11.
- vi. Studying the boron adsorption equilibrium isotherms using Langmuir, Freundlich and Redlich-Peterson models.
- vii. Investigation of the kinetics of boron adsorption by the newly prepared adsorbent using two kinetic models: pseudo first-order and pseudo second-order.
- viii. Determination of the boron adsorption mechanism on the new adsorbent using Weber and Morris intra-particle diffusion model.
- ix. Studying the boron adsorption thermodynamic and determination of its Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°).

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The following contributions are made in the present study:

- i. A new fibrous adsorbent containing glucamine capable of overcoming the challenges facing the granular resin with respect of adsorption capacity and kinetics was developed using a simplified RIGC technique based on low cost nylon-6 fibers.
- ii. Grafting of VBC onto nylon-6 fiber using RIGC is reported for the first time.

- iii. A quadratic statistical model for optimization of the reaction parameters and the density of glucamine in the adsorbent is developed.
- iv. The method developed can be extended to prepare other adsorbents based on grafting a number of acrylic and vinyl monomers onto various synthetic polymeric and natural fibers.
- v. The application of the adsorbent can also be extended to remove others soluble pollutants.

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Chapter 1 contains background of water contamination with boron and problem statement to justify the work conducted in this thesis. The objective of the thesis, the scope of work and the contribution made are also covered. This was followed by the objectives and the scopes of study. A comprehensive literature review on commercial boron-selective resins and the use of RIGC techniques for preparation of alternative polymeric adsorbents are described in chapter 2. This chapter also includes a review of previous studies pertaining boron adsorption equilibrium isotherms, kinetics and thermodynamics. Chapter 3 reveals all the materials and methods used to prepare and test the new fibrous adsorbent together with all equations used for calculations such as degree of grafting, density of functionalisation, boron adsorption capacity, boron removal efficiency and others. Chapter 4 contains the first part of the results and discussion and describes the effects of various grafting parameters on the DG and instrumental characterization of the adsorbent precursor with reference to the original nylon-6 fibers. Chapter 5 contains the second part of results and discussion. Particularly, it discusses the results of the effects of various reaction parameters on the density of glucamine incorporated in the adsorbent precursors. The results of various properties of the obtained fibrous adsorbent are also discussed in comparison with the corresponding poly(VBC) grafted precursor. Chapter 6 contains the third part of results and

discussion, which represents the performance of the newly prepared radiation grafted adsorbent with respect to adsorption capacity, equilibrium isotherms, kinetics and thermodynamics. Chapter 7 presents the overall conclusions of this study and the recommendations for future work.



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