RADIATION GRAFTED NANOFIBROUS ADSORBENT CONTAINING N-METHYL-D-GLUCAMINE FOR BORON REMOVAL

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To my beloved mother, father, and husband for all their support and understanding.

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ABSTRACT

Ion exchange resins having glucamine groups, although bearing a great potential in treating varieties of boron-containing streams have slow kinetics due to mass transfer limitations. The objective of this study is to develop a new adsorbent with a fibrous morphology that gives high adsorption capacity and fast kinetics. The new adsorbent was prepared in 3 steps involving electrospinning of poly(vinylidene difluoride) (PVDF) into nanofibres, radiation induced grafting (RIG) of glycidyl methacrylate (GMA) onto electrospun nanofibres followed by functionalisation with N-methyl-D-glucamine (NMDG). Response surface methodology (RSM) was used for optimization of PVDF electrospinning parameters allowing fibres' diameters control. Simultaneous RIG was performed with an electron beam under controlled parameters. The functionalisation reaction's parameters were also tuned with RSM to maximize the NMDG density in the adsorbent. The nanofibrous adsorbent was characterized using scanning electron microscopy, Fourier transform infrared spectrometer, differential scanning calorimetry, thermogravimetric analysis and water contact angle measurements. The performance of the adsorbent was tested for boron removal under batch and dynamic column (fixed bed) modes. The stability of the new adsorbent was confirmed by sorption/desorption tests. Nanofibrous sheets with an average fibre diameter of 350 nm were obtained at optimum voltage and concentration of 15.5 kV and 15 wt%, respectively. An optimum degree of grafting (DG) of 150% was imparted in grafted PVDF nanofibres using a 90% GMA/methanol solution and a dose of 40 kGy at a dose rate of 1.27 kGy/s. A maximum NMDG density of 2.20 mmol/g was achieved at optimum parameters of 15% NMDG concentration, 86.9 °C reaction temperature, 64.7 min and 150% DG. The new adsorbent showed 100% removal efficiency using a 0.6 g adsorbent dose within 2 h for a 100 mg/L of boron solution. The adsorption data from batch mode were best fitted to the Redlich–Peterson isotherm and the adsorption kinetics followed the pseudo-second-order. The adsorbent behaviour under dynamic conditions revealed that the breakthrough capacity is a function of both initial feed concentration and bed height whereas the flow rate marginally affected the breakthrough capacity as indicated by the 9.3% reduction with an increase of up to SV 200h^{-1}. The Thomas mathematical model was found to best fit the dynamic behaviour of the column. The adsorbent displayed a boron adsorption capacity of 17.60 mg/g-adsorbent which is 2.6 time higher than that of commercial boron selective resin such as Amberlite IRA743 (6.7 mg/g). The results of this study suggest that the adopted preparation procedure is highly effective in preparation of nanofibrous adsorbents with the desired content of boron selective ligands. Moreover, the adsorbent was proven to have a strong potential for application in boron removal from solutions as indicated by higher boron adsorption capacity and faster kinetics.

ABSTRAK

Resin pertukaran ion yang mengandungi glukamina, walaupun mempunyai potensi yang tinggi dalam merawat larutan yang mengandungi boron, umumnya mempunyai kinetik perlahan disebabkan oleh batasan perpindahan jisim. Objektif kajian ini adalah untuk mensintesis penjerap baru yang mempunyai struktur bergentian, yang boleh memberi kapasiti penjerapan yang tinggi serta kinetik pantas. Penjerap bergentian disediakan dalam 3 peringkat melibatkan kaedah elektropemejaman bagi penyediaan gentian-nano poli(vinilidena diflorida) (PVDF), pengkopolimeran cangkuk aruhan sinaran (RIG) glisidilmetakrilat (GMA) keatas gentian-nano, diikuti oleh pengfungsian dengan N-methyl-D-glukamina NMDG. Metodologi permukaan tindak balas (RSM) diaplikasikan bagi elektropemejaman PVDF untuk mengawal diameter gentian. Pencangkukan GMA ke atas gentian-nano PVDF dilakukan menggunakan kaedah RIG serentak dengan sinaran elektron. Parameter-parameter tindak balas bagi pengfungsian turut ditala menggunakan RSM untuk mendapatkan ketumpatan NMDG dalam penjerap yang maksimum. Penjerap gentian-nano dicirikan dengan menggunakan mikroskop pengimbasan elektron, spektrometer inframerah transformasi Fourier, kalorimetri pengimbasan pembezaan, analisis termogravimetri dan pengukuran sudut sentuhan air. Penilaian prestasi penjerap bergentian-nano dilakukan dalam mod berkelompok dan dinamik (lapisan tetap). Kestabilan penjerap ditentukan menggunakan kaedah penjerapan/nyaherapan. Kepingan gentian-nano berdiameter purata 350nm diperolehi masing-masing pada voltan dan kepekatan optimum 15.5 kV dan 15 wt%. Gentian–nano dengan kadar cangkukan (DG) 150% didapatkan dengan menggunakan larutan 90%GMA/metanol, pada dos 40 kGy dan kadar dos 1.27 kGy/s. Ketumpatan maksimum NMDG 2.2 mmol/g-penjerap dicapai pada kepekatan NMDG 15%, suhu tindak balas 86.86 ℃, masa tindak balas 64.66 min dan 150% DG. Kecekapan penyingkiran 100% dicapai dalam masa 2 jam, dengan menggunakan 0.6 g penjerap bergentian-nano untuk larutan yang berkepekatan 100 mg/L. Penilaian prestasi penjerap bergentian-nano menggunakan mod berkelompok menunjukkan bahawa data penjerapan paling sesuai dengan isoterm Redlich-Peterson serta mengikuti model kinetik pseudotertib kedua. Prestasi penjerap di bawah keadaan dinamik menunjukkan bahawa kapasiti penjerapan meningkat apabila kepekatan awal dan ketinggian penjerap meningkat. Didapati bahawa data eksperimen untuk kajian lajur itu mengikuti model matematik Thomas. Penjerap gentian-nano menunjukkan kapasiti penjerapan boron sebanyak 17.61 mg / g yang 2.6 kali kapasiti penjerapan resin komersil Amberlite IRA743 (6.7mg / g). Keputusan kajian ini membuktikan bahawa kaedah yang telah digunakan amat berkesan untuk digunakan bagi menyediakan penjerap bergentian-nano dengan ligan selektif boron. Di samping itu penjerap ini turut mempunyai potensi yang kuat bagi aplikasi penyingkiran boron berdasarkan kepada kapasiti penjerapan tinggi serta kinetik pantas yang diperoleh.

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LIST OF ABBREVIATIONS

AFD	-	Average fibre diameter
AMF	-	Adsorption-membrane filtration
APGDP	-	Atmospheric pressure glow discharge plasma
ATRP	-	Atom transfer radical polymerisation
BBD	-	Box–Behnken design
BSR	-	Boron selective resins
CCD	-	Central composite design
CVD	-	Chemical vapor deposition
DETA	-	Diethylenetriamine
DG	-	Degree of grafting
DMF	-	Dimethylformamide
DSC	-	Differential scanning calorimetry
DVB	-	Divinylbenzene
EB	-	Electron beam
EC	-	Electrocoagulation
ED	-	Electrodialysis
FT-IR	-	Fourier transform infrared spectrometer
GMA	-	Glycidyl methacrylate
HEP	-	1-(2-hydroxylethylamino)-2,3-propanediol
ICP-OES	-	Inductively coupled plasma optical emission spectrometry
MMA	-	Methyl methacrylate
NMDG	-	N-methyl-D-glucamine
PAN	-	Polyacrylonitrile
PEGMA	-	Poly (ethylene glycol) methyl ether methacrylate
PP	-	Polypropylene
PS	-	Polystyrene
PVA	-	Polyvinyl alcohol

PVDF	-	Poly(vinylidene fluoride)
RIGC	-	Radiation induced graft copolymerization
RO	-	Reverse osmosis
RSM	-	Response surface method
SDBS	-	Sodium dodecylbenzene sulfonate
SEM	-	Scanning electron microscopy
SV	-	Space velocity
TGA	-	Thermogravimetric analysis
THF	-	Tetrahydrofuran
TRIM	-	Trimethylolpropane trimethacrylate
WHO	-	World Health Organization

LIST OF SYMBOLS

A_R - Redlich–Peterson isotherm constant (1/mg)

C_1 - Effluent boron concentration concentration (mg/L)

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

$\Delta G°$ - Gibb's free energy change (kJ/mol)

h - Initial adsorption rate (mg/g min)

$\Delta H°$ - Enthalpy change (kJ/mol)

$\Delta H_m °$ - Melting enthalpy (J/g)

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 - Thermodynamic equilibrium constant

K_F - Freundlich adsorption constant (mg/g) $(L/mg)^{1/n}$

K_L - Langmuir adsorption constants related to adsorption energy (L/g)

K_R - Redlich–Peterson isotherm constants (L/g)

K_T - Thomas rate constant (mL/(min mg))

K_{YN} - Represents the rate constant (min^{-1}); and

M - Molecular weight (g/mol)

m - Adsorbent mass (g)

N - Number of the experimental points

Δq - Normalized standard deviation (%)

Q	-	Volumetric flow rate (L/min)
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_o	-	Adsorption capacity of the bed (mg/g)
q_t	-	Amount of boron adsorbed at t time (mg/g)
R	-	Gas constant (8.314 J/mol K)
r^2	-	Correlation coefficients
S°	-	Entropy change (J/mol K)
T	-	Temperature (K)
t	-	Time (min)
T_m	-	Melting temperature (°C)
V	-	Volume of the solution (L)
W	-	Weight (g)
W_o	-	Initial weight (g)
Wg	-	Weight of grafted samples (g)
Z_f	-	Weight of grafted samples after functionalisation (g)
Z_i	-	Weight of grafted samples before functionalisation (g)
τ	-	Represents the time required for 50% sorbate breakthrough (min)

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CHAPTER 1

INTRODUCTION

1.1 Background

Boron is a widely present drinking water contaminant known to be dangerous to the reproductive health of living organisms [1]. In nature, boron is always found bonded to oxygen or other elements forming boric acid or borates (inorganic salts). Boron exists in aquatic systems mainly in the form of non-dissociated boric acid or borate ions [2]. The presence of boron in surface water is mainly due to contamination by municipal wastewater containing industrial effluents, detergents and cleaning agents and chemical substances used for agriculture [3]. The usage of water with high levels of boron for irrigation causes these boron compounds to form complexes with heavy metal ions like Cu^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+}, leading towards higher toxicity levels compared to the original ions of the heavy metals themselves [4, 5]. Such complexes can pose a serious threat to human health and the environment when passed to groundwater. The significant rise in the use of boron compounds in various industries including nuclear technology, rocket fuel making, and production of heat-resistant materials, ceramics, glass, detergents, disinfectants, dyestuff, fertilisers, and food preservatives, has led to a substantial increase in worldwide boron production [6-8]. World boron production has increased from 4300 thousand metric tonnes in 2011 to 9400 thousand metric tonnes in 2016 [9].

In an aqueous environment, boron exists either as boric acid $B(OH)_3$ or borate anion $B(OH)^{-4}$ [10]. Boric acid is a very weak Lewis acid in aqueous solutions. It acts as an acid by accepting OH^- to form $B(OH)_4$ according to reaction 1-1 [11].

$$B(OH)_3\,(aq) + H_2O \rightleftharpoons B(OH)_4^{-} + H^+ \qquad (1\text{-}1)$$

$(Ka = 6 \times 10^{-10}, pKa\ 9.1)$

The pH of the solution plays the main role in determining which one of the two boron chemical species predominates in the aqueous solution. The boric acid species predominate at pH values between pH 7 and 9 whereas borate ions dominate at pH values from pH 9 to 11.

Boron is a necessary micronutrient for living organisms, although when consumed in higher doses it may cause toxicity. In plants, appropriate boron concentration is also needed for healthy development of crops but the gap between deficiency and excess for boron is small. The symptoms caused by high concentrations of boron in plants start with the yellowing of leaf tips that progress into the blades and burned edges on mature leaves which then causes accelerated decay and eventually the death of the plant. The severity of the symptoms vary depending on the amount of boron the plant is exposed to and the endurance of the plant. For instance, sensitive plants can tolerate only 0.3 mg/L of boron content in irrigation waters while some plants can accept boron content of up to 4 mg/L [6, 12].

Frequency and level of boron exposure influence the effects of boron on humans and animals. Boron is required in small quantities for various metabolisms of macro-nutrients in the organs. However, a chronic exposure to boron may cause damage to human organs. The effects observed thus far are cutaneous disorders, retarded growth, reproductive dangers and suspected teratogenicity [13, 14]. The presence of boron in water bodies is hazardous to living organisms and the environment, hence it is crucial to find efficient methods and techniques for its removal.

The search for efficient, cost-effective (cheaper than commercial resins) materials and robust systems for the removal of boron from different water streams is attracting worldwide attention due to the challenge posed by drinking water and waste water discharge standards on current boron-removal technologies. The standard set by the World Health Organization (WHO) was recently revised from 0.5 mg/L to 2.4 mg/L for drinking water [15]. As for wastewater, nations across the globe have set standards of not more than 4.0 mg/L [16].

Various methods have been utilised to treat streams containing different concentrations of boron. Amongst all methods, ion-exchange remains to be the most effective and efficient technology to remove boron from waters and waste waters especially when it is present in large volumes and low concentrations [5, 17]. Anion exchange resins can be used to remove boron because boron commonly exists as an anion in boric acid. However, due to the weak affinity of boric acid, a low selectivity coefficient is observed when conventional ion exchange resins are used. Furthermore, nitrate and carbonate co-existing in the solutions makes any borate that is initially adsorbed by the resin to be quickly replaced by the other anions leading to the release of borate into the treated water. Boron-selective (chelating) resins are good alternative to ion-exchange resins because the functional hydroxyl groups that they carry in the 1–2 or 1–3 positions combine with borate ions to form borate-diol complexes, resulting in a selective removal of boron from solutions. [18]. These resins are applied in ion exchange operation in a batch or continuous column mode. Batch mode adsorption is usually used to study the interaction between the adsorbent and the adsorbate. The column process is the most common and efficient ion exchange method used in the treatment of industrial wastewater.

The mechanism through which boron chelation takes place occurs through a sequence of steps according to the principles of mass transfer. Firstly, the ions diffuse through the bulk solution until they approach a stagnant layer of the solution on the exterior surface of the resin known as the boundary layer which they have to pass through. The second step is the diffusion of the ions through the gel particle of the resin. Once in the resin the ions must diffuse through restricted and water filled pores until it reaches an exchange site. The third step is the chelation of the borate ion where the ion within the resin is captured by the active group. Since the chelation process of the ions itself is thought to be very rapid, it is not the controlling factor. The rate determining step is either the first or second step i.e. the diffusion of the ions through the film or the resin particle until it reaches the exchange site. The slower of the two steps will become the rate determining step. The biggest disadvantage associated with the use of boron-selective resins is the slow kinetics of boron uptake despite their high selectivity to boric acid, in regions with neutral pH levels [16, 19]. This causes a performance limitation that has generated an immense research interest in developing boron-selective resins with improved performance in terms of higher adsorption capacity and faster adsorption kinetics.

1.2 Problem Statement

The guideline standard set by WHO for drinking water stands at 2.4 mg/L as of 2017 [20] while wastewater discharge standards for boron around the world are between 1 and 4 mg/L [16]. Many regions across the globe are struggling to meet this regulation because of the prohibitively expensive operating cost of boron selective ion exchange resins. One example of this is in Mediterranean countries, where the limited source of surface and ground waters suffer from excessive amounts of boron rendering them unusable for human or irrigation consumption [22].

In Malaysia, the problem of boron removal is profound at the landfill leachate treatment sites with boron concentration is about 7.7 mg/L [23], which requires daunting treatment to meet the regulations imposed by the Malaysian Department of Environment, which currently stands at 1 mg/L for scheduled wastewater discharge standard A [16]. Current boron removal methods employed is primarily carried out chemical precipitation using zinc sulphate and ferrous sulphate, are not efficient enough to deal with the problem. Both chemicals give only 50-65% removal for influent concentrations in the range of 150-200 ppm [24]. Besides landfill leachate treatment facilities, leachate from the integrated scheduled waste treatment facility operated by Kualiti Alam Sdn Bhd also contains a high boron concentration of up to

100 mg/L. Wastewater generated by the ceramic industry also contains a high concentration of boron, which negatively affects the environment.

There is no simple technique for boron removal where high removal efficiencies can be achieved. Most industries use a combination of different technologies such as the hybrid adsorption membrane filtration (AMF) to achieve a complete boron removal. Studies have been conducted to establish materials and technologies to decrease boron concentrations according to various standards. The following methods are currently used to meet these standards: precipitation-coagulation, adsorption on oxides, adsorption on active carbon, adsorption (on clay, fly ash and modified activated carbon) liquid-liquid extraction, electrodialysis, reverse osmosis, electrocoagulation, phytoremediation and ion exchange resins. Reverse osmosis (RO) membranes are the one of the most common technologies for boron removal and can achieve removal efficiencies of about 40-80% and over 90% in alkaline solutions with higher pH of 10-11. However, the elevated pH promotes scaling and corrosion rendering the RO method ineffective due to the membrane cost, potential for scaling and also because of the need for a multi-stage system to achieve complete removal [25, 26]. Amongst boron removal technologies, ion exchange using boron-selective resins for is most efficient technology as it provides up to 99% removal at normal conditions especially when huge volume and low concentration are dominant. One of the most commonly used commercial resin is Amberlite IRA-743 with N-methylglucamine groups, which has been in industrial use for boron removal since the 1960s [28].

Boron selective resins are highly efficient boron removers, with theoretical retention capacities reaching up to 7 mg-B/g-adsorbent, the practical capacity however depends on the flow rate and drops rapidly as flow rate increases due to mass transfer limitations and a decrease in the dynamic binding capacity of boron [29]. This is mainly due to the long diffusion path taken by the ions to reach the ion exchange sites within the resins. The main disadvantage with conventional boron selective resins is the slow kinetics during boron uptake despite their high selectivity to boric acid in regions with neutral pH levels [21, 22]. Furthermore, these resins are quite costly, and there tends to be a drop in capacity upon scaling up [23, 24]. They also have complicated regeneration processes with high chemical consumption that almost always results in capacity loss with each regeneration cycle [21]. In addition, the limited surface areas, uncontrollable structures, and hydrophobicity of these resins have made the boron selective resins less flexible and their performance unsatisfactory [25, 26].

Fibrous boron selective adsorbents are newly researched materials that have shown interesting improvement in the performance of boron removal from solutions [19, 27]. These studies used microfibres of Nylon-6 as a substrate for hosting glucamine group through grafted poly(glycidyl methacrylate) ligands. Despite the improved performance of such fibrous adsorbents, the surface area limitations due to the large diameters of around 300-800 µm remains posing a challenge for the mass transfer of boron. To mitigate the mass transfer limitations and further enhance the rapid sorption kinetics observed with microfibrous sorbents, nanofibrous containing glucamine groups is highly appealing. Nanofibres have been proposed because they have small interfibrous pore size, high permeability and more importantly is their large surface area per unit mass. The incredibly small diameters of nanofibres can potentially minimize the diffusion path of target ions and hence provide a higher specific surface area for boron chelation to occur. This in turn will result in faster sorption kinetics than in both microfibrous and commercial boron selective resins.

Among newly developed materials for boron removal, grafted and functionalised adsorbents have been proposed an alternatives to conventional resins with better performance, mainly in terms of adsorption capacity and speedy kinetics [16, 27]. Such adsorbents are prepared mainly by RIGC with high energy radiation such as electron beam or gamma rays. RIGC not only allows tuning of the properties of the adsorbent through controlling the grafting parameters but also enables desired moieties to be imparted to preformed substrates without significantly affecting their inherent properties. Thus, RIGC became an appealing method for the facile conversion of variety of substrates to resins or chelating materials [28]. Hence, it would interesting to modify polymer nanofibres with this method to incorporation side chain grafts capable of hosting boron selective groups. In this study, RIGC was used to graft glycidyl methacrylate (GMA) onto electrospun poly(vinylidene fluoride) (PVDF) nanofibres to prepare a chelating adsorbent with a glucamine moiety. Such combined procedure involving electrospinning, grafting and functionalization is unprecedented is expected to yield an adsorbent having high surface area and glucamine density. PVDF was chosen because it provided highly stable polymeric backbone that could be shaped easily into nanofibres and also because it enabled the formation of stable radicals during irradiation step [29]. GMA was used due to the presence of the oxirane ring in its structure, which provides a site for functionalisation with N-methyl-D-glucamine (NMDG) to impart the glucamine moiety through a mild ring opening reaction [30].

1.3 Objectives

The main objective of this study is to prepare a new nanofibrous adsorbent containing glucamine groups with highly improved properties for removal boron from solutions by radiation induced grafting of GMA onto electrospun PVDF nanofibres followed by NMDG treatment. The objectives can be sub-divided to the following:

i. To establish PVDF nanofibres preparation by optimisation of the electrospinning parameters.
ii. To investigate the effect of grafting reaction parameters on the degree of grafting for grafting of GMA onto PVDF nanofibres.
iii. To establsih functionalisation of poly-GMA grafted PVDF nanofibres with N-methyl-D-glucamine (NMDG) by optimisation of the reaction parameters.
iv. To evaluate the physio-chemical properties of the obtained glucamine containing nanofibrous adsorbent.
v. To investigate the performance the new adsorbent with respect to boron removal in a batch system under different operating conditions
vi. To evaluate the performance of the adsorbent for boron removal in a fixed column under different operating conditions.

1.4 Scope of Study

The scope of this study consists of five stages as depicted from the flow chart shown in Figure 1.1. The scope of work can be outlined as follows:

i. Preparation of nanofibrous mats by electrospinning of PVDF solution which was prepared by dissolving PVDF powder in methanol according to the concentrations required.

ii. Optimisation of the different parameters affecting electrospinning, including:
    - Voltage, which was varied in the range of 10-20 kV
    - Needle tip-to-collector distance, which was varied in the range of 3-15 cm
    - Concentration, which was varied in the range of 10- 20 wt%

iii. Preparation of adsorbent precursor by modification of the electrospun PVDF nanofibres using radiation induced graft polymerization of GMA onto the nanofibres to enable the introducing of functional groups to the polymeric backbone. This includes irradiation of the fibres with electron beam and investigation of the effect of the grafting parameters on the degree of grafting, including:
    - Types of solvent, which includes methanol, ethanol, propanol, butanol and pentanol.
    - Monomer concentration, which was varied in the range of 50-100 vol%.
    - Absorbed dose, which was varied in the range of 10-100 kGy.
    - Dose rate, which was varied in the range of 0.95-1.27 kGy/s

iv. The GMA grafted PVDF nanofibres were functionalised using NMDG dissolved in 1-4 dioxane to impart the ionic character to the grafted nanofibres under different reaction parameters.

v. The functionalisation parameters optimised included:
    - Concentration of NMDG, which was varied in the range of 5-15 wt%.
    - The degree of grafting of the adsorbent precursor, which was varied in the range of 80-115%.
    - Reaction time, which was varied in the range of 20-80 mins.
    - Reaction temperature, which was varied in the range of 70-90°C.

vi. Determination of the physical and chemical properties of the newly synthesised nanofibrous adsorbent with reference to the original PVDF nanofibres and GMA grafted PVDF nanofibres. 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).
    - Thermal properties, which was measured using differential scanning calorimetry (DSC)
    - Thermal stability, which was tested using thermogravimetric analysis (TGA)
    - Wettability, which was investigated using contact angle measurements.

vii. The performance of the adsorbent was tested on a batch basis and the adsorption parameters used were included:
    - Initial boron concentration, which was varied in the range of 50-200 mg/l.
    - pH, which was varied in the range of 3-11.
    - Adsorbent dosage, which was varied in the range of 0.05-1.0 g.

viii. Studying of the adsorption equilibrium isotherms using Langmuir, Freundlich and Redlich-Petterson models.

ix. Investigation of the kinetics of boron adsorption by the nanofibrous adsorbent using two kinetic models: pseudo first-order and pseudo second-order.

x. Evaluation of boron adsorption capacity of the modified nanofibres in a fixed bed column and studying the effect of different operating parameters such as concentration, flow rate and bed height. The breakthrough curves were also established for the nanofibrous adsorbents. The adsorption and desorption cycles were established.

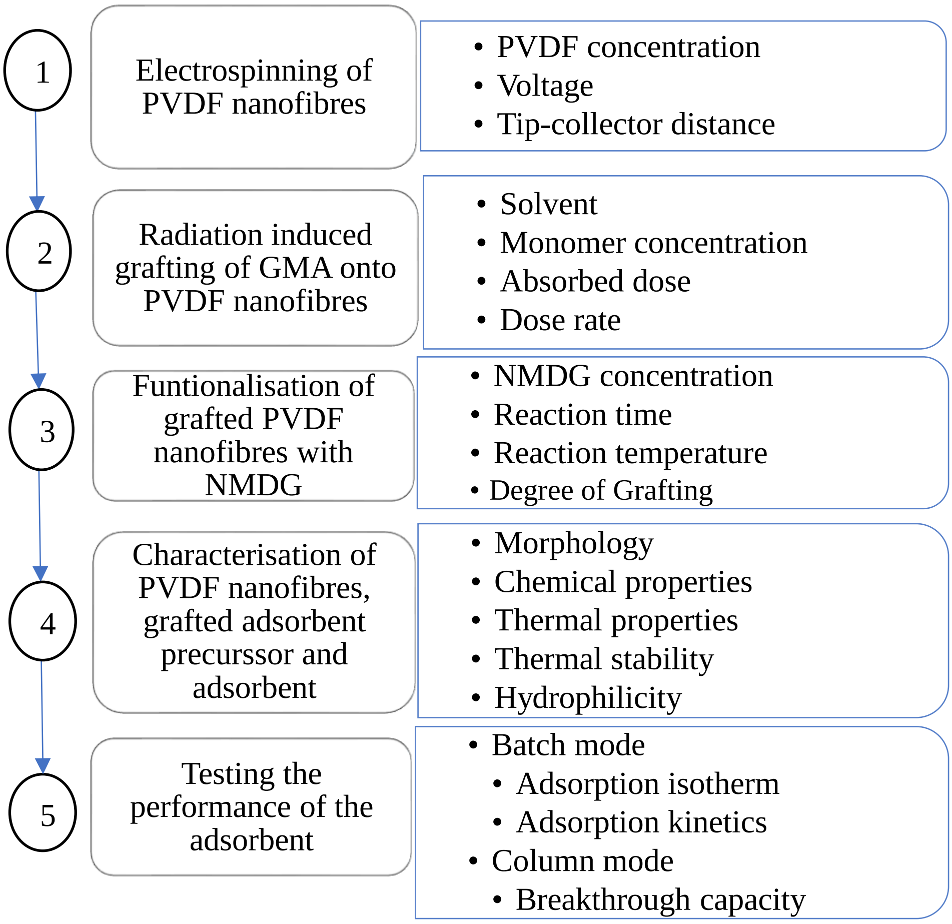

Figure 1.1: Flow chart for the scope of study.

1.5 Significance of the Study

This work provides a new glucamine-containing chelating adsorbent for boron removal possessing a nanofibrous structure, using a unique combination of two remarkable methods i.e. electrospinning and RIGC. The new nanofibrous adsorbent obtained from this study is capable of removing boron from various streams at moderate conditions. The obtained adsorbent combines not only high selectivity, due to the boron selective functional group but also a high surface area that is provided by the small fibre diameters.

The nano-structure of the adsorbent enables the development of smaller adsorbent columns with larger surface area and higher operating capacity and certainly can lead to an improvement in the economy of the process. This could certainly help not only wastewater treatment in industries but also potable water treatment plants to meet stagnant regulations imposed by environmental authorities in various countries with regards to boron concentrations in water and wastewater streams. Besides, the column filter that can be developed based on this adsorbent can be possibly used in improving domestic quality of water in work places and homes.

The electrospinning of PVDF leading to the formation of substrate mats that was used for grafting of GMA applied in water treatment in this study is rarely reported in literature. Thus, the work reported here in is an interesting contribution for electrospinning of polymers such as PVDF and their application as adsorbents. The RSM used for optimisation of electrospinning parameters provide a statistical tool to design and predict the morphology and the fibres' diameters of the nanofibres. This work also provided an opportunity to develop a quadratic statistical model for optimisation of the reaction parameters and maximisation the density of glucamine in the adsorbent. Finally, this study paves the way for the preparation of other adsorbents based on grafting of various acrylic and vinyl monomers onto various synthetic polymeric and natural fibres.

Eventually, the ultimate contribution of this study is in development of a new adsorbent with higher adsorption capacity and faster kinetics than commercial resins and microfibrous adsorbent, which allows treatment of bigger boron contaminated water volumes at shorter time. This study will also allow the establishment of sorption isotherms, sorption kinetics and mechanism of adsorption for boron adsorption by the new nanofibrous boron selective adsorbent. This study also allows determination of the most suitable combination of parameters for the three main phases of this study which are electrospinning of PVDF, radiation induced grafting of GMA onto PVDF nanofibres and functionalisation of the nanofibres.

1.6 Thesis Outline

The current thesis is presented in 5 chapters. Chapter 1 is an introduction that covers background of the study and problem statement and describes objectives, scope and significance of the study. In Chapter 2, a comprehensive literature review including boron removal techniques and their advantages and limitations, electrospinning and its parameters and applications, radiation induced grafting, and nanofibre characterisation techniques is given. Chapter 3 contains the methodology used for fabrication, modification and for the characterisation and testing of nanofibres for boron adsorption. In Chapter 4 the results are presented and discussed with reference to previous works, obtained data are analysed and interpreted. Chapter 5 includes the final conclusions and some recommendations to improve the work in future studies.

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