UNIVERSITI PUTRA MALAYSIA

NITRATE AND FLUORIDE ADSORPTION FROM AQUEOUS SOLUTION BY CHEMICALLY MODIFIED PALM KERNEL SHELLS

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FK 2016 10

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By

MUHAMMAD TARIQ BASHIR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

September 2016

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DEDICATION

Dedicated to my Mother ‘Rehmat Bibi” who left me 15 years back to whom I loved too much. Allah may keep her soul in peace and Jannat- ul Firdaus (Ameen).

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

NITRATE AND FLUORIDE ADSORPTION FROM AQUEOUS SOLUTION BY CHEMICALLY MODIFIED PALM KERNEL SHELLS

By

MUHAMMAD TARIQ BASHIR

September 2016

Chairman : Associate Professor Salmiaton Binti Ali, PhD
Faculty : Engineering

Nitrate (NO_3^{-1}) and fluoride (F^{-1}) are widespread contaminants in drinking water sources in many countries including Pakistan and detrimental to human health. Palm kernel shell (PKS) is available in abundance in Malaysia as an agricultural waste that can be modified into a water treatment adsorbent by enhancing its affinity to remove anions. This research studied the current NO_3^{-1} and F^{-1} concentrations in Southern Punjab, Pakistan because there is no monitoring and adequate water treatment system in this region to provide drinking water to the public that is safe and free from pollutants (especially NO_3^{-1} and F^{-1}). Out of 248 samples of drinking water sources in Southern Punjab Pakistan, 11.69% and 8.1% were badly contaminated with NO_3^{-1} and F^{-1}, respectively.

An eco-friendly and feasible adsorbent "Chemically Modified Palm Kernel Shell (CMPKS)" was prepared in a two-step process. Firstly, ground PKS particles were exposed to hydroxyl pre-treatment (mercerization) using potassium hydroxide to remove impurities and make the particles porous. Subsequently, the mercerized PKS was quaternized by grafting of N-(3 Chloro-2 Hydroxypropyl) trimethylammonium chloride (CHMAC) under alkaline conditions. Batch studies were conducted to determine the adsorption of nitrate and fluoride on CMPKS at varying contaminant concentrations, adsorbent doses, temperature and pH. Subsequently, the experimental data were simulated using isotherm models, including the Langmuir, Freundlich and Redlich-Peterson models. The adsorption capacity of 54.18 mg/g and 2.35 mg/g was achieved for nitrate and fluoride, respectively. A series of batch tests were also conducted to simulate the adsorption kinetics and thermodynamics of NO_3^{-1} and F^{-1} removal. Based on the goodness of fit of pseudo-second order model, Elovich Equation and results from the thermodynamic study, the adsorption process was classified as physical adsorption with exothermic and endothermic nature of reactions for nitrate and fluoride, respectively with slight degree of chemisorption. Further, the regenerated CPMKS retained 97% and 98% of its adsorption capacity for nitrate and fluoride, respectively even after five adsorption-regeneration cycles. The sorption capacities and kinetics of the novel CMPKS (adsorbent) in a single and

binary system were studied in a continuous flow advanced multi-columns design (AMCD). The sorption capacities were studied in fixed beds and stratified layered columns beds (SLCB). The SLCB shows enhanced efficacy for single and two-component solutions in AMCD. The resulting data were interpreted using the Adams-Bohart and Thomas models, which showed good agreement with the experimental data. Finally, the physicochemical characteristics of CMPKS were determined using scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller analysis, proximate and chemical analyses, and carbon-hydrogen-nitrogen elementary analysis as well as surface charge on CMPKS.

In conclusion, the cheap and abundant PKS biomass with two-step chemically modification has excellent potential in removing nitrate and fluoride contaminants in water. In addition, the modified PKS has robust properties and strength which can be reused and regenerated for longer usage in adsorption process to treat contaminated water with nitrate and fluoride pollution. Subsequently, this shall reduce the operating and capital cost of the treatment process and very suitable for poor countries.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENJERAPAN NITRAT DAN FLUORIDA DARIPADA LARUTAN AKUES MELALUI PENGUBAHSUAIAN TEMPURUNG ISIRUNG KELAPA SAWIT SECARA KIMIA

Oleh

MUHAMMAD TARIQ BASHIR

September 2016

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Nitrat (NO_3^{-1}) dan fluorida (F^{-1}) merupakan pencemar yang biasa terdapat dalam sumber air minuman di kebanyakan negara termasuk Pakistan dan memudaratkan kesihatan manusia. Tempurung isirung kelapa sawit (PKS) boleh didapati dengan banyaknya di Malaysia sebagai sisa pertanian yang boleh diubah suai menjadi penjerap rawatan air dengan penambahan afinitinya untuk menyingkirkan anion. Penyelidikan ini bertujuan untuk mengkaji kepekatan semasa NO_3^{-1} dan F^{-1} di Punjab Selatan, Pakistan kerana tiada pemantauan dan tiada sistem rawatan air yang mencukupi di rantau ini untuk menyediakan air minuman yang selamat dan bebas daripada bahan pencemar (terutamanya NO_3^{-1} dan F^{-1}) kepada orang ramai. Daripada 248 sampel dari sumber air minuman di kawasan ini, 11.69% dan 8.1% telah tercemar dengan teruk oleh NO_3^{-1} dan F^{-1}, masing-masing.

Bahan penjerab mesra alam dan tersaur "Tempurung Isirung Kelapa Sawit Diubah Suai Secara Kimia (CMPKS)" telah disediakan dalam proses dua langkah. Pertama, zarah PKS hancur didedahkan kepada pra-rawatan hidroksil (*mercerization*) menggunakan kalium hidroksida untuk menyingkirkan kekotoran dan menjadikan zarah berliang. Selepas itu, PKS merserais telah di'q*uaternized*' oleh cantuman N-(3 Kloro-2 Hidrosipropil) Trimetilamonium Klorida (CHMAC) dalam keadaan alkali. Kajian kelompok telah dijalankan untuk menentukan penjerapan nitrat dan fluorida ke atas CMPKS pada pelbagai kepekatan bahan cemar, dos penjerap, suhu dan pH. Seterusnya, data eksperimen telah disimulasikan menggunakan model isoterma, termasuk model Langmuir, Freundlich dan Redlich-Peterson. Kapasiti penjerapan nitrat sebanyak 54.18 mg/g dan 2.35 mg/g telah dicapai untuk nitrat dan fluoride, masing-masing. Satu siri ujian kelompok juga dijalankan untuk mensimulasikan kinetik penjerapan dan termodinamik penyingkiran NO_3^{-1} dan F^{-1}. Berdasarkan kebagusan penyesuaian model tertib pseudo-kedua, persamaan Elovich dan hasil kajian termodinamik, proses penjerapan ini boleh diklasifikasikan sebagai penjerapan fizikal dengan sifat tindakbalas eksoterma dan endoterma untuk nitrat dan fluorida, masing-masing dengan sedikit darjah pengkimierapan. Tambahan lagi,

CMPKS terjana semula mengekalkan 97% dan 98% daripada kapasiti penjerapan untuk nitrat dan fluorida, masing-masing, walaupun selepas lima kitaran penjerapan-penjanaan semula. Kapasiti serapan dan kinetik CMPKS novel (penjerap) dalam sistem tunggal dan perduaan telah dikaji dalam aliran berterusan reka bentuk pelbagai turus termaju (AMCD). Kapasiti serapan dikaji dalam lapisan tetap (*fixed bed*) dan lapisan turus berlapis berstrata (*stratified layered column bed*) (SLCB). SLCB menunjukkan keberkesanan dipertingkatkan untuk larutan satu dan dua-komponen dalam AMCD. Data yang terhasil telah ditafsirkan menggunakan model Adams-Bohart dan Thomas, yang menunjukkan penjanjian yang baik dengan data eksperimen. Akhir sekali, ciri-ciri fizikokimia CMPKS telah ditentukan dengan menggunakan mikroskopi elektron penskanan, spektroskopi tenaga penyerakan X-ray, spekstroskopi inframerah transformasi Fourier, analisis Brunauer-Emmett, analisis proksimat dan kimia, dan analisis unsur karbon-hidrogen-nitrogen serta caj permukaan ke atas CMPKS.

Kesimpulannya, biojisim PKS yang murah dan banyak dengan dua langkah pengubahsuaian kimia mempunyai potensi yang sangat baik dalam menyingkirkan nitrat dan fluorida dalam air. Di samping itu, PKS yang diubahsuai mempunyai ciri-ciri yang teguh dan kekuatan yang boleh diguna semula dan dijana semula untuk penggunaan berpanjangan dalam proses penjerapan untuk merawat air yang tercemar dengan nitrat dan fluorida. Ini kemudiannya akan mengurangkan kos operasi dan modal proses rawatan dan sangat sesuai untuk negara-negara miskin.

ACKNOWLEDGEMENTS

At first, thanks to Almighty Allah, the most beneficial and merciful who helped me to conduct this research. I wish and pray that this research, though meagre may help millions of people who are suffering from chronic diseases and dying due to nitrate and fluoride contamination. For me, this research journey was a fight against nitrate and fluoride contamination.

My appreciation, respect and gratefulness are directed to my supervisory committee members for providing inspiration. Especially appreciative to Prof..Madya Dr. Salmiaton binti Ali, chairperson of my research committee, for observing the potential and value of this work. Her consistent moral support and freedom of work is an unforgettable asset that helped me to work with innovative ideas.

I would also extend my special thanks to Professor Dr. Azni Idris, whose critiques during presentations and meetings taught me to cope with words of wisdom. His philosophy of research can help a student to catch one rabbit rather than chasing two rabbits, because the person who chases two rabbits catches neither.

I would also like to state my deep gratitude to Dr. Razif Harun and Dr. Mohsen Nourouzi for their encouragement and guidance throughout this research, which was invaluable to a foreigner in the prosperous country of Malaysia. I am also thankful to Universiti Putra Malaysia for financial support for this study. Moreover, it is particularly gratifying to have assistance from the academic and non- academic members of Universiti Putra Malaysia. Moreover, I would extend my thanks to management of Asian College of Technology, Bahawalpur, Pakistan and Sadiqabad College of Technology, Sadiqabad, Pakistan who provided invaluable involvement in the overall research. I would be dishonest, if don't appreciate Miss Sue of Evergreen who always helped me beyond the scope of her duty.

Last, but not the least, I am thankful to my family, and especially to my wife and daughters, Manahil Bashir and Nidahil Bashir, who suffered a lot during this extended period of my research journey. They always provided inspiration for me to excel as the way to progress in life and overcome the frustration. I wish Almighty Allah may help them in their future endeavors.

I certify that a Thesis Examination Committee has met on 26th of September 2016 to conduct the final examination of Muhammad Tariq Bashir on his thesis entitled "NITRATE AND FLUORIDE ADSORPTION FROM AQUEOUS SOLUTION BY CHEMICALLY MODIFIED PALM KERNEL SHELLS" in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998.The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

AE	Anion exchanger
AMCD	Advanced multi-columns design
AR	Anion resins
AW	Agricultural waste
BET	Brunauer, Emmett and Teller
BJH	Barrett, Joyner and Halenda
C_e	Equilibrium concentration (mg/L)
CHMAC	N-(3 Chloro-2 hydroxypropyl) trimethylammonium chloride
CHN	Carbon, Hydrogen and Nitrogen
C_i	Initial concentration of adsorbate (mg/L)
C_{ims}	Initial concentration in two-component solution (Nitrate and Fluoride) (mg/L)
CMPKS	Chemically Modified Palm Kernel Shell
C_t	Concentration of adsorbate at time 't'(mg/L)
d_{Av}	Average Diameter
EBCT	Empty bed contact time (min)
EDX	Energy Dispersive X-Ray
FT-IR	Fourier Transform Infrared Spectroscopy
K_1	Pseudo first order constant (min^{-1})
K_2	Pseudo Second Order Constant (g mg^{-1} min^{-1})
K_{ab}	Adams-Bohart rate constant (L mg^{-1} min^{-1})
K_f	Freundlich isotherm constant (mg/g)
K_{th}	Thomas rate constant (L mg^{-1} min^{-1})
M	Mean concentration (mg/L)

N_o	Concentration at saturation in Adams-Bohart Model (mg/L)
pH_{pzc}	Point of zero charge
PKS	Palm Kernel Shell
PVC	Polyvinyl chloride
q_e	Adsorption at equilibrium (mg/g)
Q_o	Langmuir monolayer adsorption capability (mg/g)
q_s	Maximum sorption in column (mg/g)
q_{th}	Thomas adsorption capacity (mg/g)
R	Universal gas constant (J/mol K)
R_L	Langmuir separation factor
SD	Standard deviation
SEM	Scanning Electron Microscopy
SLCB	Stratified Layered Column Bed
TCS	Two-Component Solution
V_{av}	Average Volume
V_L	Linear velocity (cm/min)
w/w	Ratio weight by weight
WS	Wheat Straw
ΔG^o	Change in Gibbs free energy (kJ/mol)
ΔH	Change in enthalpy (kJ/mol)
ΔS	Change in entropy (kJ/mol)

CHAPTER 1

INTRODUCTION

1.1 Foreword

Nitrate and Fluoride contamination in natural water resources has emerged as a global issue since last few decades (Ansari and Parsa, 2016; Gu et al., 2013; Jia et al., 2015; Jordão et al., 2002; Sowmya and Meenakshi, 2014). Elevated levels of nitrate and fluoride have been reported in Pakistan, India, Sri Lanka, China, Taiwan, Iran, African's countries, Canada, the United States and many more (Azizullah et al., 2011; Chaudhary et al., 2010; Manjappa et al., 2003). The issue of simultaneous prevalence of both fluoride and nitrate at higher levels is even more threating in Pakistan, India, and China (Avtar et al., 2013; Khan et al., 2013; Liu et al., 2014; Mekonen and Kumar, 2001). According to WHO, more than 260 million populace are expected to have a supply of water contaminated with fluoride (Amin et al., 2014; WHO, 2013) and millions of people are exposed to nitrate contaminated water (WHO, 2013).

Nitrate contamination of groundwater usually occurs in arid and semi-arid zones around the world where water resources are recharged slowly, and the use of irrigation is extensive (Kazemi, 2011; Tagma et al., 2011). Nitrate and other nitrogenous compounds are essential for life process; however, elevated nitrate concentration in ground and surface water may also pose a serious threat to living organisms (Khan et al., 2013; Zhou et al., 2012). The major cause of excessive accumulation of nitrate is leaching processes from agricultural lands. The level of nitrates in the groundwater is normally small, but leaching and other processes increase the concentration until it reaches a critical level. Prior to the widespread use of nitrogenous fertilizers, nitrogen in the soil was primarily enriched by leguminous plants. Due to the presence of cyanobacteria in their root nodules, these plants have the ability to fix atmospheric nitrogen. However, extensive use of nitrogenous fertilizer has contaminated surface water and ground water. Undeniably, fertilizers account for the major source of nitrate contamination, numerous other sources like human and animal wastes, lack of good sanitary practices and improper drainage system also have contributed to the nitrate contamination of surface and groundwater (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013).

Fluoride occurs naturally in most water sources across the globe. It exists in abundance in the earth's crust, and can reach groundwater by natural phenomena (Fawell, 2006; Koteswara and Mallikarjun, 2014). Fluoride also occurs naturally in public water systems mostly because of the runoff from the weathering of rocks containing fluoride or compounds of fluorine and also the erosion and the leaching of soils into groundwater (Tahir and Rasheed, 2013). Moreover, the deposition is usually facilitated by the solubility of fluoride mineral as well as its availability, the speed of water flow, temperature, pH, and also the concentration of bicarbonate ions

and calcium in the water. In addition, the industries also contribute greatly to fluoride occurrence in groundwater (Koteswara and Mallikarjun, 2014).
The conventional treatment plant does not remove nitrate and fluoride (Ayoob et al., 2008; Sharma, 2003; Vardhan and Karthikeyan, 2011). Due to high solubility, the nitrate and fluoride ions removal need advanced treatment methods that use enhanced pressure and temperature, or catalysts, are usually required (Crist et al., 1996; Dagwa et al., 2012; Ibrahim, 2013; Sowmya and Meenakshi, 2014). Many technologies for nitrate and fluoride removal in waters are reported based on ion exchange (Ayoob et al., 2008; Lin and Wu, 1996; Samatya et al., 2006), membrane filtration (Schoeman, 2009; Sehn, 2008), chemical and biological methods and adsorption (Bhatnagar and Sillanpää, 2011; Chen et al., 2012; Kumar and Chakraborty, 2006; Ma et al., 2014; Xu et al., 2012). Undeniably, the treatment processes of nitrate and fluoride from natural waters are complicated due to variation in pH level.

Moreover, exceptional research has been reported for removal of nitrate and fluoride in a single and binary component system. Mekonen and Kumar (2001) have developed a mechanism for integrated removal using a combination of biological and physiochemical approach. Apart from its effectiveness, it is complex and expensive technique. Hence, it is a consistent problem for researchers to develop the eco-friendly treatment methods with minimum limitation considering health issues related to water.

Recently, to address the scarcity of safe drinking water in many countries, adsorbents have been developed that can remove anions such as nitrate and fluoride from water. The adsorbents (bioadsorbents) prepared from various agricultural wastes by chemical modification are attractive due to the widespread availability of wastes and the efficiency, economy and environmentally friendly nature of both the adsorbents and their preparations. The pine sawdust and bark, wheat straw, wheat stalk, tea waste and rice husk and alike were used to prepare adsorbents for removal of nitrate and fluoride by grafting cation group (Cai et al., 2015; Keränen et al., 2013; Loganathan et al., 2013b; Singh et al., 2008; Xu et al. 2010; Vardhan and Karthikeyan, 2011; Yadav et al., 2013).

The processing and production of palm oil yield sufficient amount of biomass including palm kernel shell, empty fruit bunches, and mesocarp fiber. Almost 90 % of this biomass is discarded as waste that can be further utilized in developing useful by-products with the help of modern and eco-friendly technologies (Awalludin et al., 2015). Palm kernel shell (PKS) contains organic compounds like holocellulose, lignin, and extractives (Awalludin et al., 2015; Edmund et al., 2014; Jong and Tang, 2015). Moreover, due to exceptional chemical composition and ionic strength, PKS can also be modified to enhance its affinity for removal of dye namely, Reactive Black 5 (Koay et al., 2014; Nourouzi et al., 2009). Unlikely, exceptional or no research is reported for removal of nitrate and fluoride in a single or binary system from drinking water using adsorbent prepared by chemical modification of palm kernel shell. Moreover, exceptional research has been conducted to remove nitrate and fluoride in a column packed with stratified/or coarse layers of the adsorbent

having different sizes. This has led to extensive research study for the new and economical process to modify PKS for removal of nitrate and fluoride from water obtained from available drinking water sources.

1.2 Environmental and Health Issues

The drinking water with high nitrate content can be detrimental to human health and WHO has recommended a maximum acceptable concentration of 10 mg/L as N (45 mg/L) in drinking water (EPA, 2011; Maherry et al., 2010; Mahmood et al., 2007; WHO, 2011). Infants under six months are susceptible to nitrate contamination as it causes methemoglobinemia, commonly called as a blue baby syndrome (Gu et al., 2013; Mizuta, 2004; Sowmya and Meenakshi, 2014). Millions of children die every year due to blue baby syndrome (Azizullah et al., 2011). In humans, nitrate toxicity may cause brain disorder, development of thyroid hypertrophy and cancer of digestive tract (Buzalaf et al., 2012; Loganathan et al., 2013a). Nitrate toxicity in humans is due to the reduction of nitrate to nitrite in the body. Nitrite so formed reacts with secondary and tertiary amines and amides derived from food and other sources to form dimethylnitrosamines that are potent carcinogens (Tomar and Kumar, 2013; WHO, 2011).

Fluoride ion, being negatively charged attracted by the positively charged calcium ion in the human body (Mahmood et al., 2007). As a result of this strong electronegativity of fluoride ion, it is widely associated with different kinds of fluorosis. Fluoride in low concentrations causes dental caries, especially in children. On another hand, its presence in excess of 1.5 mg/L can give rise to dental fluorosis. The substantial increase in concentration cause fluorosis that can have serious effects on skeletal tissue of human as well, with antagonistic changes in bone structures (Fawell et al., 2006; Schmoll, 2013). Hence, the recommended guideline value for fluoride concentration is 1.5 mg/L in drinking water (EPA, 2011; WHO, 2013). Furthermore, if fluoride intake is excessive, it can go a long way to interfere with the metabolism carbohydrates, vitamins, minerals and protein. This can also impede the creation of DNA in the body and thereby leading to numerous other negative effects. A number of studies reported that fluoride is directly or indirectly responsible for most of the kidney diseases (Liu et al., 2014; Tahir and Rasheed, 2013; Tomar and Kumar, 2013). It can also interfere with the function of the brain and associated with a high level of morbidity causing various diseases including bladder and different other kinds of cancer, arthritis, brittle bones, brain damage, alzheimer syndrome, osteoporosis, thyroid disorder and infertility (Mondal and George, 2015; Sankararamakrishnan, Sharma and Iyengar, 2007; Singh et al., 2008; Yu et al., 2015).

1.3 Problem Statement

Health issues occurring due to high nitrate and fluoride levels in drinking water are a widespread problem on the globe including Pakistan. Therefore, the need for

concerted research efforts aimed at developing water treatment method that can help combat the problem of elevated levels of these contaminants in available drinking water. Although a number of studies are available that are reported in peer-reviewed literature, most of these have been conducted in setting differing what exist in developing nations. Only a few of these studies have been conducted in Pakistan despite the aging problem of elevated contaminant concentration in available drinking waters. This complexity is the fact that a number of the treatments that have been earlier reported are expensive and may not be feasible options for poor nation settings. The use of biological approaches in treating water with high levels of nitrate and fluoride has also been suggested by some quarters. However, there are inherent complications associated with this approach owing to technical difficulties involved. Moreover, issues related to high cost of treatment call for the need for alternative treatment option such as chemical treatment using the economical raw material.

PKS possess increased hardness and stiffness having less probability to be compressed in the columns and subsequent pressure drop that makes it a feasible option. Thus, the current study hopes to explore the possibility of adopting a chemical approach involving adsorption using palm kernel shell (PKS) as a precursor for the purification of water with elevated levels of nitrate and fluoride. The prepared adsorbent should possess sufficient positive charge to attract and adsorb negatively charged ions such as nitrate and fluoride In this context, KOH has been reported as more effective activating agent for few natural materials such as rice husk (Muniandy et al., 2014) and peanut hull (Chowdhury, 2013), but no research has been reported on mercerization of PKS with KOH. The reactivity of the potassium metal may exhibit greater effectiveness than NaOH during activation by reducing carbon content (Muniandy et al., 2014; Sudaryanto et al., 2006) and can provide increased positive sites (nitrogen content) for anions by subsequent reaction with cationic groups. Moreover, KOH requires a small amount of energy with low impact on the environment so as to reduce volatile matters available in the agro-based precursor (Cao et al., 2006; Chowdhury, 2013). Furthermore, acetylation of mercerized PKS can further reduce hydrophobicity helping in absorption of cationic compounds. In addition, acetylation can minimize the susceptibility of the swelled PKS to biological decay (Mokaloba and Batane, 2014; Mwaikambo and Ansell, 1999).

1.4 Objective of the Research

The main objectives formulated for this research are as follows:

1. To conduct an assessment based on laboratory investigations, current levels of nitrate and fluoride in available drinking water sources in selected areas of Southern Punjab, Pakistan identified in prior available data,

2. To chemically modified palm kernel shell for removal of elevated levels of nitrates and fluoride using sustainable and eco-friendly approach,

3. To examine the mechanism and evaluate effectiveness of prepared bioadsorbent for removal of nitrate and fluoride and develop statistically significant correlations that may exist between treatment efficiency by the adsorbent as well as assessment at various temperatures.

4. To develop an experimental design of continuous flow columns packed with fixed and course/ or stratified bed at lab-scale for removal of elevated levels of nitrates and fluoride in single and binary system.

1.5 Scope of the Research

Nitrate and Fluoride are manifesting in drinking water sources and pose serious health issues in many countries throughout the world. Hence, to keep clarity, scope of this research is summarized based on objectives as follows:

1. This study evaluated current levels of the nitrate and fluoride contamination in drinking water sources in the Southern Punjab region of Pakistan.

2. Chemically modified palm kernel shell (CMPKS) was prepared by grafting N-(3 Chloro-2 Hydroxypropyl) trimethylammonium chloride (CHMAC) on mercerized palm kernel shell (PKS) with KOH without using a catalyst. The physiochemical properties of PKS and CMPKS were characterized to validate the efficacy by SEM, EDX, FTIR, BET surface area, CHN elemental analysis, proximate analysis and chemical analysis as well as a surface charge on the adsorbent.

3. The data were generated in batch study to predict the capability of CMPKS as an adsorbent in the removal of nitrate and fluoride at pH 6 and 7. The obtained data was further assessed by Langmuir, Freundlich and Redlich-Peterson isotherm models, pseudo-first and second order models, as well as Weber-Morris diffusion model. In addition, the adsorbent capacity should be recoverable so that the material can be reused a number of times. Hence, the CMPKS was regenerated and reused repeatedly. Moreover, applicability of the adsorbent was studied at different temperature and subsequently, thermodynamic parameters for nitrate (NO_3^{-1}) and fluoride (F^{-1}) were determined to predict the nature of the adsorbent process.

4. The continuous flow multi-column system was designed to depict nitrate and fluoride sorption considering single and binary system in a fixed and stratified bed. The stratified columns containing different particle sizes were evaluated for separate and simultaneous (i.e., single and binary solutions) removal of nitrate and fluoride. The effect of the size of particles in column sorption, flow rate, initial contaminant concentrations, and depth were also considered in this part of the research. Subsequently, the composition of a mixture or stratification of different sizes of particles was defined to attain optimum adsorption in Advanced Multi-Column Design (AMCD). The generated data were analyzed by Thomas and Adams-Bohart model.

1.6 Organization and Outline of Thesis

This research thesis is organized in five parts, and essentially, first three chapters comprised of an introduction, literature review and material and methodology. Chapter 1 delineates the background of this study as well as environmental and health issues associated with nitrate and fluoride. Chapter 2 encompasses the current prevailing situation in main Asian countries and available treatment techniques for removal of these contaminants. Adsorption that is considered as the best treatment method is evaluated for its efficacy. Subsequently, different adsorbent and adsorption techniques are demonstrated with a particular focus on biomaterials or in other word, adsorbents prepared from agricultural wastes. In the third chapter, study area investigated is explained and a brief review of materials, chemicals, and equipment used to prepare chemically modified palm kernel shell (CMPKS) are discussed with a theoretical description that are used in this research.

The fourth part of this document delineates the results and discussion and further sub-grouped into chapter 4, 5 and 6 to keep clarity and due to a significant difference in research approach and outcomes. Finally, chapter 7 accomplishes the research outcomes and recommendations for future working.

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