UNIVERSITI PUTRA MALAYSIA

REMOVAL OF COPPER AND IRON BY AMIDOXIME MODIFIED POLY (ACRYLONITRILE-G-MICROCRYSTALLINE CELLULOSE)

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By

MOHAMMAD BIN ABDULLAH

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DEDICATION

This thesis is dedicated to my family, colleague, students and friends that always support me whenever I need all of you during completing this PhD journey.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Heavy metal ions that not treated from many industries have been severely polluted the environment and can caused serious impact to human health. The discharge of heavy metal effluents into water sources can generate accumulation of toxicity and unwanted contaminants. Hence, proper treatment of heavy metal ions from industrial wastewater is a main environmental pollution concern for consideration. The adsorption process become an alternate approach to eradicate heavy metal ions. This study investigated the polymer-based adsorbent; amidoxime modified poly(acrylonitrile-*g*-microcrystalline cellulose) that was used to remove selected heavy metal ions (copper, Cu^{2+} and iron, Fe^{2+}) by adsorption method. The poly(acrylonitrile-*g*-microcrystalline cellulose) was synthesised by redox polymerisation of acrylonitrile (AN) and microcrystalline cellulose (MCC) monomer and further modified chemically with amidoxime to produce AO modified poly(AN-g-MCC) adsorbent. Then, single batch adsorption experiments for each heavy metal, Cu^{2+} and Fe^{2+} were executed at different working conditions such adsorbent dosage, pH, initial metal ion concentrations and soaking time. Besides, batch mode of adsorption for binary heavy metal ions onto AO modified poly(AN-*g*-MCC) was studied.

The synthesised of poly(AN-*g*-MCC) produced the highest yield (96%) at polymer ratio 93:7 (AN:MCC). The characterisations result of polymerised polymer; Fourier transform infrared (FTIR) confirmed the successful of polymerisation due to the presence of absorption peaks that were assigned to the C≡N and –COOH functional groups on the spectra. Scanning Electron Microscope (SEM) showed the appearance of AN bead onto MCC surface. The thermogravimetric (TG) analysis recommended that the thermal stability of poly(AN-*g*-MCC) was lower as compared with MCC. The poly(AN-*g*-MCC) where further chemically altered with hydroxylamine hydrochloride. The FTIR spectra verified the successful conversion of C≡N into amidoxime groups. The microanalysis presented that the overall trend of elemental percentage for AO modified poly(AN-*g*-MCC) copolymers were increase of nitrogen and hydrogen elements. To further confirm the quantity of amidoxime functional group in modified polymer, the amine capacity test

was conducted. The ratio of 93:7 has the highest amount of amine capacity (12.42 mmol/g), followed by 90:10 (11.45 mmol/g) and the low amount of amine capacity at feed mole ratios 95:5 (10.5 mmol/g) and 97:3 (9.75 mmol/g).

The single batch system of the adsorption progression for the elimination of Cu^{2+} and Fe^{2+} were conducted by varying the pH (2 -12), adsorbent dosage (0.2 – 1.0 g), initial metal ion concentration (50-150 mg/L) and contact time (2-100 minutes). The maximum removal percentage for Cu^{2+} and Fe^{2+} were 99.5% and 96.4%, respectively at pH 7. The effect of adsorbent dosage showed the 1.0 g/L of adsorbents, result the highest percentage of Cu^{2+} (99.8%) and Fe^{2+} (88.63%) correspondingly. The highest percentage removal of Cu^{2+} and Fe^{2+} were 99.5% and 95.8% respectively at 50 mg/L.

Meanwhile at 60 minutes the percentage removal become maximum for Cu^{2+} (89.0%) and Fe^{2+} (87.5%). The experiment data were examined using equilibrium and kinetic studies. Equilibrium data was well fitted with Freundlich isotherms. The Freundlich isotherms showed good agreement for the adsorption of Cu^{2+} (R^2 of 0.9493) with the maximum adsorption capacities of 120.58 mg/g. The adsorption of Fe^{2+} also satisfied with Freundlich isotherms (R^2 of 0.9558) with maximum adsorption capacities of 235.91 mg/g.

In binary system, the effects of adsorbent dosage (0.2-1.2 g), pH (3,5, and 9), initial adsorbate concentration (20-100 mg/L) and contact time (0-100 minutes) on equilibrium adsorption capacity were determined. An increase in adsorbent dosage increased the removal of metal ions in binary system. The Cu^{2+} and Fe^{2+}uptake was more favourable at pH 9 in binary system. The percentage removal of Cu^{2+} at 100 mg/L of binary solution was 91.13 %, whereas the Fe^{2+} ions uptake was only 84.51%. Both heavy metal ions reached their equilibrium at 60 min and after that the removal of heavy metal ions become almost constant. Extended Langmuir model and extended Freundlich model provide a suitable description of the experimental binary data. The comparison of the single and binary isotherms reveals an antagonistic interaction (occurred when the adsorption capacity of an adsorbent reduces in a solution containing other components) between the Cu^{2+} and Fe^{2+}. In addition, pseudo-second-order model was found suitable for the description of adsorption kinetic for both metal ions onto AO modified poly (AN-*g*-MCC), for both single and binary system, signifying chemisorption between adsorbent and heavy metals molecule.

Based on experimental findings, AO modified poly (AN-*g*-MCC) polymer is a promising functional regenerable adsorbent with high capacity to remove heavy metal (for single and binary system) from liquid environment

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Doktor Falsafah

PENYINGKIRAN KUPRUM DAN BESI OLEH POLI (AKRILONITRIL-G-SELULOSA MIKROKRISTAL) DIMODIFIKASI DENGAN AMIDOKSIM

Oleh

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Ion logam berat yang tidak dirawat dari kebanyakan industri telah mencemarkan alam sekitar dengan teruk dan boleh menyebabkan kesan yang serius kepada kesihatan manusia. Pembuangan efluen logam berat ke dalam sumber air dapat menghasilkan pengumpulan toksik dan bahan cemar yang tidak diingini. Oleh itu, rawatan yang betul terhadap ion logam berat dari air sisa industri menjadi tarikan utama dalam punca pencemaran alam sekitar. Proses penjerapan menjadi pendekatan alternatif untuk merawat ion logam berat. Kajian ini mengkaji penyerap berasaskan polimer; amidoksim poli(akrilonitril-*g*-selulosa mikrokristal) yang diubahsuai dan digunakan untuk menyingkirkan ion logam berat terpilih (Kuprum, Cu^{2+} dan Ferum, Fe^{2+}) dengan kaedah penjerapan. Kopolimer poli(akrilonitril-*g*-selulosa mikrokristal) disintesis dengan pempolimeran redoks, monomer akrilonitril (AN) dan selulosa mikrokristal (MCC) selanjutnya dimodifikasi secara kimia dengan amidoksim untuk menghasilkan penjerap poli(AN-*g*-MCC) yang dimodikasi dengan amidoksim (AO). Kemudian, eksperimen penjerapan secara tunggal untuk setiap logam berat, Cu^{2+} dan Fe^{2+} dilaksanakan pada keadaan parameter yang berbeza seperti dos penjerap, pH, kepekatan ion logam awal dan masa rendaman. Selain itu, kaedah penjerapan mod kumpulan untuk ion logam berat kationik binari terhadap AO-dimodifikasi poli(AN-*g*-MCC) telah dikaji.

Poli(AN-*g*-MCC) tersintesis menghasilkan hasil tertinggi (96%) pada nisbah polimer 93:7 (AN:MCC). Hasil pencirian polimer terpolimer; Inframerah transformasi Fourier (FTIR) mengesahkan kejayaan pempolimeran kerana kehadiran puncak penyerapan yang ditetapkan kepada kumpulan berfungsi C≡N dan –COOH pada spektrum. Mikroskop Elektron Pengimbasan (SEM) menunjukkan bentuk AN manik pada permukaan MCC. Analisis termogravimetrik (TG) mengesyorkan bahawa kestabilan terma poli(AN-*g*-MCC) adalah lebih rendah berbanding dengan MCC. Poli(AN-*g*-MCC) di mana selanjutnya diubah secara kimia dengan hidroksilamin hidroklorida. Spektrum FTIR mengesahkan penukaran berjaya C≡N ke dalam kumpulan amidoxime. Analisis mikro menunjukkan bahawa aliran keseluruhan peratusan unsur untuk kopolimer poli (AN-*g*-MCC) diubah suai AO ialah peningkatan unsur nitrogen dan hidrogen. Untuk

mengesahkan lagi kuantiti kumpulan berfungsi amidoxime dalam polimer yang diubah suai, ujian kapasiti amina telah dijalankan. Nisbah 93:7 mempunyai jumlah kapasiti amina tertinggi (12.42 mmol/g), diikuti oleh 90:10 (11.45 mmol/g) dan jumlah kapasiti amina yang rendah pada nisbah mol suapan 95:5 (10.5 mmol/g).) dan 97:3 (9.75 mmol/g).

Proses penjerapan untuk penyingkiran Cu^{2+} dan Fe^{2+} dalam sistem penjerapan tunggal telah dilakukan dengan mengubah pH (2-12), dos bahan penjerap (0.2 -1.0 g), kepekatan awal ion logam (50-150 mg/L) dan masa tindak balas (2-100 minit). Peratusan penyingkiran maksimum bagi Cu^{2+} dan Fe^{2+} masing-masing ialah 99.5% dan 96.4% pada pH 7. Pengaruh dos bahan penjerap menunjukkan pada 1.0 g/L dos bahan penjerap, menghasilkan peratusan tertinggi Cu^{2+} (99.8%) dan Fe^{2+} (88.63%) yang sepadan. Peratusan tertinggi penyingkiran Cu^{2+} dan Fe^{2+} masing-masing ialah 99.5% dan 95.8% pada kepekatan awal 50 mg/L. Manakala pada minit ke 60 peratusan penyingkiran menjadi maksimum bagi Cu^{2+} (89.0%) dan Fe^{2+} (87.5%). Data eksperimen diuji menggunakan kajian keseimbangan dan kinetik. Data keseimbangan dilengkapi dengan isoterma Langmuir dan Freundlich. Isoterma Freundlich menunjukkan penerangan yang baik untuk penjerapan Cu^{2+} (R^2 =0.9493) dengan kapasiti penjerapan maksimum 120.58 mg/g. Penjerapan Fe^{2+} juga mematuhi isoterma Freundlich (R^2=0.9558) dengan kapasiti penjerapan maksimum 235.91 mg/g.

Dalam sistem penjerapan binari, kesan dos bahan penjerap (0.2-1.2 g), pH (3,5, dan 9), kepekatan awal ion logam (20-100 mg/L) dan masa rendaman (0-100 minit) ke atas proses penjerapan keseimbangan kapasiti telah ditentukan. Peningkatan dos bahan penjerap meningkatkan penyingkiran ion logam dalam sistem binari. Penyerapan Cu^{2+} dan Fe^{2+} adalah lebih baik pada pH 9 dalam sistem binari. Peratusan penyingkiran Cu^{2+} pada 100 mg/L larutan binari ialah 91.13 %, manakala penyerapan ion Fe^{2+} hanya 84.51%. Kedua-dua ion logam berat mencapai keseimbangannya pada minit ke 60 dan selepas itu penyingkiran ion logam berat menjadi hampir sekata. Model Lanjutan Langmuir lanjutan dan Model Lanjutan Freundlich memberikan penerangan yang sesuai mengenai data eksperimen binary. Perbandingan isoterma tunggal dan binari mendedahkan interaksi antagonis (berlaku apabila kapasiti penjerapan bahan penjerap berkurangan dalam larutan yang mengandungi lebih dari satu komponen) antara Cu^{2+} dan Fe^{2+}. Sebagai tambahan, model susunan kedua-pseudo didapati sesuai untuk mengambarkan kinetik penjerapan bagi kedua-dua ion logam terhadap AO-dimodifikasi poli(AN-*g*-MCC), bagi system tunggal dan system binari. Hal ini bagi menandakan penjerapan kimia antara molekul penjerap dan molekul logam berat.

Berdasarkan hasil dapatan eksperimen ini, polimer AO-dimodifikasi poli(AN-*g*-MCC), merupakan penjerap terfungsi yang berpotensi untuk dijana semula dengan kapasiti yang tinggi bagi menyingkirkan bahan logam berat (untuk persendirian dan berterusan) daripada bahan cecair persekitaran.

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LIST OF SYMBOLS

C_0	Initial dye concentrations	mg/L
C_e	Equilibrium dye concentrations	mg/L
C_{IPD}	Boundary layer thickness effect	-
C_t	Equilibrium dye concentrations at any time *t*	mg/L
k_1	Pseudo-first-order adsorption rate constant	1/min
k_2	Pseudo-second-order rate constant	mg/g min
K_F	Freundlich constant	(mg/g) (L/mg) $1/_n$
K_{IPD}	Intraparticle diffusion rate constant	mg/g min
K_L	Adsorption equilibrium Langmuir constant	L/mg
m	Mass of adsorbent	g
N	number of data points	-
n	Surface heterogeneity	Dimensionless
$q_{e\,(cal)}$	Calculated adsorption capacity	mg/g
$q_{e\,(exp)}$	Experimental adsorption capacity	mg/g
q_e	Adsorption capacity at equilibrium	mg/g
q_{max}	Maximum adsorption capacity	mg/g
q_t	Adsorption capacity at any time *t*	mg/g
R	universal gas constant	8.314 J/mol K
R^2	Correlation coefficient	-
R_L	Separation factor	Dimensionless
SSE	Sum of squares errors	-
T	Absolute temperature	K
V	Volume of dye solution	L
α	Elovich sorption rate constant	mg/g min
β	Elovich constant correspond to extent of surface coverage	g/mg

LIST OF ABBREVIATIONS

AN	Acrylonitrile
AO	Amidoxime
BET	Brunauer-Emmett-Teller
CFU	Colony forming unit
CHNS	Carbon, hydrogen, nitrogen and sulphur
Cu^{2+}	Copper Ions
DMF	Dimethylformamide
EtOH	Ethanol
Fe^{2+}	Iron Ions
FTIR	Fourier transform infrared
IPD	Intra Particle Diffusion
KPS	Potassium persulphate
MCC	Microcrystalline cellulose
MtOH	Methanol
PAN	Poly(acrylonitrile)
PFO	Pseudo-first-order
Poly(AN-*g*-MCC)	Poly(acrylonitrile-*g*-microcrystalline cellulose)
PSO	Pseudo-second-order
SBS	Sodium bisulphate
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis

CHAPTER 1

INTRODUCTION

1.1 Research background

Water is essential for humans, animals and plants for their daily life. Facts stated that 70% of earth land is waterlogged areas. However, lack of clean water is the main problem with the increase in human populace, urbanization and pollution in the world. According to United Nations World Water Development Report 2021, the recent status needs for the upgrading water resources supervision. Billions of people do not have safe drinking water even though the access to improved drinking water was already expanded. Apart from that, the modification of the water cycle will also pose hazards for energy production, food safety, human fitness, economic growth and poverty saving, thus extremely threatening the accomplishment of the Sustainable Development Goals (United Nations 2021). About 2 billion people live in countries suffering high water anxiety, and about 4 billion people experience severe water shortage during at least one month of the year (United Nations 2019).

Water pollution usually refers to chemicals or other materials in concentrations greater than would occur under natural conditions. The water pollution can occur once unwanted materials enter into water that eventually changes the quality of water (Feng et al., 2020). This water contaminants, include microbes, nutrients, heavy metals, organic chemicals, oil and sediments, can be a pollutant. Contaminants are typically the cause of major water quality degradation around the world.

The pollution of water with the heavy metals from a variety of industries has become a serious environmental problem for many years. Some industries produce varying concentrations of heavy metal overloaded waste streams with significant consequences for any receiving environmental sections. According to Afolabi et al., (2021), one of the main sources of water pollution are generated from industrial effluents. The wastewater from industrial activities such as manure sludge, agricultural waste effluents and environmental vicissitudes are the main sources of these contaminants. These impurities comprise toxic heavy metals, dyes, pesticides, organic compounds, fertilizers and etc. Preisner (2020) also reported, about untreated industrial waste that are discharged into water sources. The amassing of heavy metals discharge has bad effects on the health of biotic and abiotic components such as flora, fauna, and human alike (Kovacova et al., 2019). Among these industrial wastes were industrial fertilizer, catalysts, gear, magnets, airbag valves, electronics, tooth protects, exhaust smoke, stainless steels etc. (Feng et al., 2020). Mineral pollutants most commonly appearing in wastewater effluents are nickel, zinc, silver, lead, iron, chromium, copper, arsenic, cadmium, and uranium. The contaminants of metallic wastes are expected from industrial growth and some of them are consuming as nutrients both for plants and human beings in a small amount (Briffa et al., 2020). However, if these species are present outside the tolerance limits, these are reported to affect the human and environmental health harmfully (Zakaria et al., 2021). In Malaysia, the standard of effluent release was restricted by the Department of

Environment (DOE) in the Third Schedule Environmental Quality Act, 174 as attached in Appendix A.

In order to resolve the heavy metals problems mentioned above, different techniques were employed, such as ion exchange, membrane technology, chemical coagulation and precipitation, electrolytic reduction and adsorption (Ida and Eva, 2021) (Demcak et al., 2017). Several methods such using an activated carbon (León et al., 2020), and aluminum salt (Zafra-Mejía et al., 2020) consume high energy, not eco-friendly, highest in costing and hazard to human. Because of that reason, many researchers come out with new adsorbents that can be used which is more economical and safer to an environment.

In recent years, the application of chelating sorbents in emerging sturdy complexes with heavy metal ions has been considered in more perspective (Younas et al., 2021). The active nitrile (AN) groups present in polyacrylonitrile (PAN) copolymers allow presenting new functional groups by different reactions. There were a few different techniques of modifications of PAN fibers to obtain cathionite, anionite, and ampholyte (Dang et al., 2020). Sruthi et al., (2020) had studies the surface modifications of PAN with sodium hydroxide to get a significant number of carboxylic groups. In the present study, the alteration of PAN with hydroxylamine was carried out to form hydroxy-functionalized resins. The adsorbent based on polyacrylonitrile and microcrystalline cellulose (MCC) were prepared and this resin present reactive suspended groups (cyano groups) that can be modified by different types of substances such as hydroxylamine (Petrovic et al., 2021, Zahri et al., 2015), hydrazine (Sruthi et al., 2020), ethylenediamine (Subri et al.,2020) and thiosemicarbazide (Noruzi et al., 2020, Deng et al., 2016) by nucleophilic addition and cycloaddition reactions. Microcrystalline cellulose was chosen because it shown a good physicochemical possession such as crystallinity, moisture content, surface area, porosity and molecular weight (Viera-Herrera et al., 2020).

1.2 Problem statement

Due to hasty industrialization and development nowadays, our environment suffers with large quantity of dangerous and excessive heavy metals that are released with unfitting pretreatment. Many industries such as plating, metal smelters, alloy, mining, microelectronics, battery, plastics manufacturers consist of heavy metals contamination in their waste streams (Younas et al., 2021). Apart from that, agricultural effluents consist of heavy metals source like fertilizers and pesticides are intensively used. A major concern in industrial operations especially in wastewater treatment is to meet with the discharge regulation. A few methods employed for the removal of heavy metals ions from polluted and contaminated water become highly expensive in cost, ineffective, produce hazardous material to the environment, and sometime become toxic to human and animals. The feasible procedures that can considered as economical and multi-functional selective sorbents was develop as a research focus for several decades.

The most obvious sign of water pollution is heavy metals. The problem of heavy metal pollution in water needs constant monitoring and investigation as these elements do not degrade and incline to bio-magnify in human through food chain (Ali et al., 2019). The

formation of cutting-edge and cost-effective treatment methods is anticipated for well cleanup of heavy metal encompassing wastewater and recovery of water resources. The modified microcrystalline cellulose as adsorbent (AO modified poly (AN-*g*-MCC)) has a broad range of physicochemical properties (such higher crystallinity indexes, rough surfaces, particle with micro sized, and improved thermal stability, Beroual et al., (2021)) that make them particular attractive as separation media for wastewater treatment and water purification (Viera-Herrera et al., 2020). After modification, they are fixed with dual functional groups which gave it the capability to selectively adsorb heavy metals to its surface more efficient than ordinary activated carbon. The successful accomplishment of this research may solve challenges associated with the development of industrial workable and adequate functional polymer-based adsorbents for heavy metal containing effluent treatment.

1.3 Research Goals and Objectives

The main goal of this project is to study the efficacy of newly developing functional polymeric adsorbent, AO modified poly(AN-*g*-MCC), for adsorptive removal of heavy metals from aqueous solution. These goals would be succeeded via the following objectives as follows:

i. To prepare poly(acrylonitrile-*g*-Microcrystalline cellulose) (poly(AN-g-MCC)) copolymer with different feed mole ratios and chemically modified it with amidoxime (AO).

ii. To investigate the uptake of copper (Cu^{2+}) and iron (Fe^{2+}) solutions onto amidoxime-modified poly(AN-*g*-MCC) from aqueous solution in a single batch adsorption system.

iii. To examine the adsorptive capacity, equilibrium and kinetics of AO modified poly(AN-*g*-MCC) adsorbent for binary heavy metals (Cu^{2+} and Fe^{2+}) adsorption from aqueous solution in batch operations.

1.4 Scope of the Study

This study focused on the preparation and application of AO modified poly (AN-*g*-MCC) as a potential large-scale polymer-based adsorbent to segregate heavy metals in industrial wastewater. Influence of several operating parameters, such as adsorbent dosage, initial heavy metals concentration, pH, and contact time on the adsorptive heavy metal removal efficacy of the polymeric adsorbents would be inspected.

Adsorption studies are frequently inadequate to batch experimentations with single component contaminant (Yousef et al., 2020), which do not offer suitable scale up data for probable multicomponent industrial scale wastewater treatment. Few works have reported the binary adsorption study of heavy metal ions in treating wastewater effluent. Thus, this research also focuses on assessing the binary adsorption of copper (Cu^{2+}) and

iron (Fe^{2+}) from aqueous solution in a batch system. Effect of a few variables (pH, initial heavy metal concentrations, contact time and adsorbent dosage) on binary heavy metal adsorption were observed. The isotherm and kinetic study were also examined for this binary system for Cu^{2+} and Fe^{2+} adsorption.

1.5 Novelty of Research Study

The modified functional polymeric adsorbent has a wide range of physicochemical properties that make them frequently attractive as separation and reactive tools for wastewater treatment and water purification. Industrial wastewaters effluent contains more than one heavy metal component. However, to date, the application of AO modified poly(AN-*g*-MCC) polymer in batch and binary systems toward Cu^{2+} and Fe^{2+} ions has not been reported elsewhere. Thus, in the present study, evaluation of binary adsorption system was carried out using functional amidoxime modified poly(AN-*g*-MCC) adsorbent. The mechanism of Cu^{2+} and Fe^{2+} ion adsorption onto AO modified poly(AN-*g*-MCC) polymer and adsorbent regeneration were investigated in detail.

1.6 Thesis layout

In order to complete the objectives of this study, the following scopes of work have been specified. This thesis consists of 6 chapters, organized as:

- Chapter one (1): Introduction, provides a general introduction on heavy metals bearing wastewater and brief review about the treatment methods, associated problems, objectives, novelty and research scope.

- Chapter two (2): Presents detail literature review related to modification polymer and its application in heavy metals uptake from the aquatic environment.

- Chapter three (3): Explanation about the procedure for polymer synthesis, modification, as well as adsorption experimentation are highlighted.

- Chapter four (4): Results and discussion concerning polymer yields, characterisation, and its preliminary application in removing copper and iron ions.

- Chapter five (5): Results and discussion of single copper and iron ions adsorption studies and analysis are reported here. The study of desorption and regeneration also briefly reported here for single adsorption. The discussion of binary copper and iron ions adsorption studies and analysis are also reported here.

- Chapter six (6): Conclusion and recommendations, this part recap the obtained research findings, limitations and suggestions for feasible future work.

REFERENCES

Ab Razak N. H., Praveena S. M., Aris A. Z., & Hashim Z. (2015). Drinking water studies: A review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia). *Journal of Epidemiology and Global Health.* 5 (4), 297-310.

Abbaspour N, Hurrell R. & Kelishadi R. (2014). Review on iron and its importance for human health. *J Res Med Sci*.,19(2):164-174.

Abdullah, M., Majid, R. A., Abdullah, L. C., Abdul-Wahab, M. F., Aziz, M. Q. F. A., Sabri, N. H. Hamdan, M. SA., Zaiton, S. N. A., & Muhamad, S. H. A. (2018). Functionalization of polyacrylonitrile-grafted cellulose with amidoxime and its antimicrobial property. *AIP Conference Proceedings*. 2045, 020042.

Abdullah, M., Sukor, M.Z., Roslan, A., & Tumar, M. (2016). Preliminary Study of Adsorption Copper (II) Ions from Aqueous Solution Using Aromatic Green Dwarf Waste as an Biosorbent. *J. Appl. Environ. Biol. Sci.,* 6(7S):58-62.

Abesekara, M. S., Kosvinna, K. N. R. & Amarasinghe, B. M. W. P. K. (2020). Adsorption and desorption studies of Ni^{2+} ions on to coconut shell char. *IOP Conf. Series: Earth and Environmental Science*, *427*, 012005

Abualnaja, K. M., Alprol, A.E., Abu-Saied, M. A., Mansour, A. T. & Ashour, M. (2021). Studying the Adsorptive Behavior of Poly (Acrylonitrile-co-Styrene) and Carbon Nanotubes (Nanocomposites) Impregnated with Adsorbent Materials towards Methyl Orange Dye. *Nanomaterials,* 11, 1144.

Adeyi, A. A., Jamil, S. N. A. M., Abdullah, L. C., Choong, T. S. Y., Lau, K. L. & Abdullah, M. (2019). Simultaneous adsorption of cationic dyes from binary solutions by Thiourea-Modified Poly(acrylonitrile-co-acrylic acid): Detailed isotherm and kinetic studies. Materials, 12, 2903.

Adeyi, A. A., Jamil, S. N. A. M., Abdullah, L. C., Choong, T. S. Y., Lau, K. L. & Abdullah, M. (2019). Adsorptive removal of methylene blue from aquatic environments using thiourea-modified poly(acrylonitrile-co-acrylic acid). *Materials, 12*, 1734.

Adeyi, A., A., Jamil, S., N., A., M., Abdullah, L., C., Choong, T., S., Y., Lau, K., L., Abdullah, M. (2019). Adsorptive removal of methylene blue from aquatic environments using thiourea-modified poly (acrylonitrile-co-acrylic acid). *Materials,* 12(11), 1734.

Afolabi, O., F., Musonge, P., & Bakare, F., B., (2021). Bio-sorption of copper and lead ions in single and binary systems onto banana peels. *Cogent Engineering*, 8:1,1886730.

Ahamad, K. U., Singh, R., Baruah, I., Choudhury, H., & Sharma, M.R. (2018). Equilibrium and kinetics modeling of fluoride adsorption onto activated alumina, alum and brick powder, *Groundwater for Sustainable Development*, *7*;452-458.

Ahmad Zaki, F., & Abdullah, I. (2015). Graft Copolymerization of Acrylonitrile onto Torch Ginger Cellulose. *Sains Malaysiana,* 44(6), 853–859.

Ajay, K. M., Kiran, C. R. & Mishra, G. K. (2010). Removal of heavy metal ions from aqueous solutions using chemically (Na_2S) treated granular activated carbon as an adsorbent. *Journal of Scientific & Industrial Research, 69*; 449-453.

Akbar, N., A., Abdul Aziz, H., & Adlan, M., N. (2015). Iron and Manganese Removal from Groundwater using High Quality Limestone. *Applied Mechanics and Materials*., 802, 460-465.

AkI, M., A., Yousef, A., E., F., M., & Abd El-nasser, S. (2013). Removal of Iron and Manganese in Water Samples Using Activated Carbon Derived from Local Agro-Residues. *Journal of Chemical Engineering & Process Technology,* 4:4.

Akpomie, K. G., Dawodu, F. A., & Adebowale, K. O. (2015). Mechanism on the sorption of heavy metals from binary-solution by a low-cost montmorillonite and its desorption potential. Alexandria Engineering Journal,54:757–767.

Al-Asheh, S., Banat, F., Al-Omari, R., & Duvnjak, Z., (2000). Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. *Chemosphere,* 41:659-665.

Albayati, T. M., Sabri, A. A., & Abed, D. B. (2019). Adsorption of binary and multi heavy metals ions from aqueous solution by amine functionalized SBA-15 mesoporous adsorbent in a batch system. Desalination and Water Treatment, 151:315–321.

Alghamdi, A.A., Al-Odayni, A-B., Saeed, W.S., Al-Kahtani, A., Alharthi, F.A., & Aouak T. (2019). Efficient Adsorption of Lead (II) from Aqueous Phase Solutions Using Polypyrrole-Based Activated Carbon. *Materials*,12, 2020.

Ali A. F., & Abd Ali Z. T. (2020). Sustainable Use of Concrete Demolition Waste as Reactive Material in Permeable Barrier for Remediation of Groundwater: Batch and Continuous Study. *Journal of Environmental Engineering*, 146 (7): 04020048.

Ali H., Khan E., & Ilahi I. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*, Article ID 6730305, 14 pages

Ali M. R., Hamad H. A., Hussein M. M. & Malash G. F. (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. Ecological Engineering, (91) 317-332.

Al-Qahtani, K.M. (2016). Water purification using different waste fruit cortexes for the removal of heavy metals. *Journal Am. Sc*., *11* (11) 198-203.

Al-Shannag, M., Al-Qodah, Z., Bani-Melhem, K., Qtaishat, M., R., & Al Kasrawi, M., (2015). Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance. *Chemical Engineering Journal,* 260, 749-756.

Amphol Daochalermwong, Napassorn Chanka, Kriangsak Songsrirote, Peerapan Dittanet, Chalida Niamnuy, & Anusorn Seubsai (2020). Removal of heavy metal ions using modified celluloses prepared from pineapple leaf fiber. *ACS Omega*, *5* (10), 5285-5296.

Anayet, K., Dunlop, M., Acharya, B., Bissessur, R. & Ahmed, M. (2018). Polymeric composites with embedded nanocrystalline cellulose for the removal of iron (II) from contaminated water. *Polymers, 10*(12), 1377.dong

Argawal S.K. (2009). Heavy metal pollution. Darya Ganj, New Delhi:S.B. Nangia, APH Publishing Corporation.

Asfaram, A., Ghaedi, M., Goudarzi, A., & Rajabi, M. (2015). Response surface methodology approach for optimization of simultaneous dye and metal ion ultrasound-assisted adsorption onto Mn doped Fe_3O_4-NPs loaded on AC: kinetic and isothermal studies. *Dalton Trans*., 44(33), 14707-14723.

Ashfaq, A., Clochard, M-C., Coqueret, X., Dispenza, C., Driscoll, M. S., Ulański, P. & Al-Sheikhly, M. (2020). *Polymers*, 12, 2877.

Ashraf, S., Ali, Q., Zahir, Z. A., Ashraf, S., & Asghar, H. N. (2019). Phytoremediation: environmentally sustainable way for reclamation of heavy metal polluted soil. *Exotox. Environ. Safe*. 174, 714-727.

Azimi, A., Azari, A., Rezakazemi, M., & Ansarpour, M., (2017). Removal of Heavy Metals from Industrial Wastewaters: A Review. *ChemBioEng Review,* 4 (1) 37-59.

Balintova, M., Petrilakova, A., & E. Singovszka, E., (2012). Study of metal ion sorption from acidic solutions. *Theor Found Chem Eng,* 46, 727–731.

Barskiy, D.A., Tayler, M.C. & Marco-Rius, I. (2019). Zero-field nuclear magnetic resonance of chemically exchanging systems. *Nat Commun,* 10, 3002.

Bart, H. J. & von Gemmingen, U. (2005). Ullmann's encyclopedia of industrial chemistry. Weinheim, DE: Wiley-VCH Verlag.

Bera, T., Mohanta, N., Prakash, V., Pradhan, S., & Acharya, SK. (2019). Moisture absorption and thickness swelling behaviour of luffa fibre/epoxy composite. *Journal of Reinforced Plastics and Composites*, 38 (19-20):923-937.

Beroual, M., Boumaza, L., & Mehelli, O. (2021). Physicochemical Properties and Thermal Stability of Microcrystalline Cellulose Isolated from Esparto Grass Using Different Delignification Approaches. *J. Polym Environ*, 29, 130-142.

Bhanu, V. A., Rangarajan, P., Wiles, K., Bortner, M., Sankarpandian, M., Godshall, D., Glass, T. E., Banthia, A. K., Yang, J., Wilkes, G., Baird, D. & McGrath, J. E. (2002). Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors. *Polymer*, 43, 4841-4850.

Bhattacharya, A. & Misra, B., N. (2004). Grafting: A versatile means to modify polymers. Techniques, factors and applications. *Progress in Polymer Science*, 29, 767-814.

Binod K. Chaudhary and James Farrell (2014). Preparation and Characterization of Homopolymer Polyacrylonitrile-Based Fibrous Sorbents for Arsenic Removal. Journal of Environmental Engineering Science. 31(11): 593–601.

Bohli, T., Ouederni, A. & Villaescusa, I. (2017). Simultaneous adsorption behavior of heavy metals onto microporous olive stones activated carbon: analysis of metal interactions. *Euro-Mediterranean Journal for Environmental Integration,* 2:19.

Bouchoum, H., Benmoussa, D., Jada, A., Tahiri, M., & Cherkaoui, O. (2019). Synthesis of amidoximated polyacrylonitrile fibers and its use as adsorbent for Cr (VI) ions removal from aqueous solutions. *Environmental Progress & Sustainable Energy*, 38 (5), 13196.

Boulaiche, W., Hamdi, B., & Trari, M. (2019). Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamic studies. *Applied Water Science* 9:39,

Briffa, J., Sinagra, E., & Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*, 6 (2020) e04691.

Butler, J. A.V. & Ockrent, C. (1930a). Studies in electrocapillarity Part I. The electrocapillarity curves of organic acids and their salts. *Journal of Physic Chemistry*, 34 (10), 2286-2296.

Cai, J., Ding, W. M., & Wang, Y. M. (2016). Adsorption of copper ion by modified sawdust. Chinese Journal of Environmental Engineering,10: 7109–7113.

Calvet, R., (1989a) Analyse du concept de biodisponobilité d'une substance dans le sol. *Sci Sol* 26 (3): 183–201.

Camara, M., Jamil, N.R. & Abdullah, A.F.B. (2019). Impact of land uses on water quality in Malaysia: a review. *Ecol Process* 8, 10.

Carlmark, A., Larsson, E, & Malmström, E. (2012). Grafting of cellulose by ring-opening polymerisation – A review. *European Polymer Journal* 48(10):1646–1659.

Carneiro, J., Döll-Boscardin, P. M., Fiorin, B. C., Nadal, J. M., Farago, P. V., & de Paula, J. P. (2016). Development and characterization of hyaluronic acid-lysine nanoparticles with potential as innovative dermal filling. *Brazilian Journal of Pharmaceutical Sciences*, 52 (4): 645-651.

Cegłowskia, M., Gierczyka, B., Frankowskia, M. & Popendab, L. (2018). A new low-cost polymeric adsorbent with polyamine chelating groups for efficient removal of heavy metal ions from water solutions. *Reactive and Functional Polymers. 131*, 64-74.

Chen, J. J., Ahmad, A. L. & Ooi, B. S. (2013). Poly (N-isopropylacrylamide-co-acrylic acid) hydrogels for copper ion adsorption: Equilibrium isotherms, kinetic and thermodynamic studies. Journal of Environmental Chemical Engineering. 1 (3): 339-348.

Chen, J., J., Ahmad, A., L., & Ooi, B., S. (2013). Poly (N-isopropylacrylamide-co-acrylic acid) hydrogels for copper ion adsorption: Equilibrium isotherms, kinetic and thermodynamics studies. *Journal of Environmental Chemical Engineering*, 1(3), 339-348.

Chen, Y., C., & Tzu, H., K., (2018). Evaluation of Acid Leaching on the Removal of Heavy Metals and Soil Fertility in Contaminated Soil. *Hindawi Journal of Chemistry*, Volume 2018, Article ID 5036581, 8 pages,

Chen, Z., Zhang, J., Fu, J., Wang, X., Han, R., & Xu, Q. (2014). Adsorption of methylene blue onto poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) nanotubes: Kinetics, isotherm and thermodynamics analysis. *Journal of Hazardous Materials*, 273, 263-271.

Choi, S., H., & Nho, Y., C. (2000). Adsorption of UO_2^{2+} by polyethylene adsorbents with amidoxime, carboxyl and amidoxime/carboxyl group. *Radiation Physics and Chemistry*, 57, 187-193.

Cimá-Mukul, C. A., Abdellaoui, Y., Abatal, M., Vargas, J., Santiago, A. A., & Barrón-Zambrano, J. A. (2019). Eco-Efficient Biosorbent Based on Leucaena leucocephala Residues for the Simultaneous Removal of Pb (II) and Cd (II) Ions from Water System: Sorption and Mechanism. *Bioinorganic chemistry and applications*, 2814047.

Crawford, R., L., (1981). Lignin biodegradation and transformation. New York John Willey and Sons' ISBN 978-0-471-05743-7/.

Cruz, J., K., & Diaz, L., J. (2019). Adsorption of Cu (II) onto Fe (III)- Modified Montmorillonite- Kinetic, Isotherm and Thermodynamic Studies. *IOP Conference Series: Materials Science and Engineering*, 540 012004.

d'Halluin, M., Rull-Barrull, J., Bretel, G., Labrugere, C.,Le` Grognec, E. & Felpin, F. X. (2017). Chemically modified cellulose filter paper for heavy metal remediation in water. *ACS Sustainable Chem. Eng*., *5*, 1965−1973.

Dahou, W., Ghemati, D., Oudia, A., & Aliouche, D. (2010). Preparation and biological characterization of cellulose graft copolymers. *Biochemical Engineering Journal*, 48, 187-194.

Dai, D., & Fan, M. (2010). "Characteristic and Performance of Elementary Hemp Fibre," *Materials Sciences and Applications*, 1 ,6: 336-342.

Dang, W., Liu, J., Wang, X., Yan, K., Zhang, A., Yang, J., Chen, L., & Liang, J., (2020). Structural Transformation of Polyacrylonitrile (PAN) Fibers during Rapid Thermal Pretreatment in Nitrogen Atmosphere. *Polymers*,12,63.

Dastbaz, A. & Keshtkarb, A. R. (2014). Adsorption of Th^{4+}, U^{6+}, Cd^{2+}, and Ni^{2+} from aqueous solution by a novel modified polyacrylonitrile composite nanofiber adsorbent prepared by electrospinning. *Applied Surface Science*, 293: 336-344.

Dehouche, N., Kaci, M., Idres, C., & Bruzaud, S. (2021). Filler Content Effect on Water Uptake and Thermal Stability of Poly(3-Hydroxybutyrate-Co-3-Hydroxyhexanoate) /Microcrystalline Cellulose Biocomposites. *Macromolecular Symposia*, 396 (1).

Demcak, S., Balintova, M., Hurakova, M., Frontasyeva, M., V., Zinicovscaia, I., & Yushin, N. (2017). Utilization of poplar wood sawdust for heavy metals removal from model solutions. *Nova Biotechnol. Chim*, 16, 26–31,

Deng, S., Wang, P., Zhang, G., & Dou, Y. (2016). Polyacrylonitrile-based fiber modified with thiosemicarbazide by microwave irradiation and its adsorption behavior for Cd (II) and Pb (II). *Journal of hazardous materials*, 307. 10.1016/j.jhazmat.2016.01.002.

Desta, M., B. (2013). Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste. *Journal of Thermodynamics, Volume* 2013, Article ID 375830, 6 pages.

Dinari M., Mohammadnezhad G., Soltani R. (2016). Fabrication of poly (methylmethacrylate)/Silica Kit-6 nanocomposite via in situ polymerization approach and their application for the removal of copper (II) ions from aqueous solution. *RSC Adv. 6*,11419–11429.

Dolgormaa, A., Lv CJ, Li, Y., Yang, J., Yang, J., X., Chen, P., Wang, H., P., & Huang, J., (2018). Adsorption of Cu (II) and Zn (II) Ions from Aqueous Solution by Gel/PVA-Modified Super-Paramagnetic Iron Oxide Nanoparticles. *Journal Molecules,* 15-23.

Dong, Y., Han, Z., Liu, C. & Du, F. (2010). Preparation and photocatalytic performance of Fe (III)-amidoximted PAN fiber complex for oxidative degradation of azo dye under visible light irradiation. *The Science of the Total Environment*, 408: 2245-2253.

Dongxiao, O., Zhuo, Y., Hu, L., Zeng, Q., Hu, Y. & He, Z. (2019). Research on the adsorption behavior of heavy metal ions by porous material prepared with silicate tailings. *Journal of Minerals*, *9*, 291.

Ehsan Bahojb Noruzi, Behrouz Shaabani, Silvano Geremia, Neal Hickey, Patrizia Nitti & Hossein Samadi Kafil. (2020). Synthesis, Crystal Structure, and Biological Activityof a Multidentate Calix [4] arene Ligand Doubly Functionalized by 2-Hydroxybenzeledene-Thiosemicarbazone. *Molecules*, 25, 370;

Ejikeme, P., M., Okoye, A., I., & Onukwuli, O., D. (2011). Kinetics and Isotherm Studies of Cu^{2+} and Pb^{2+} Ions Removal from Simulated Waste Water by Gambeya Albida Seed Shell Activated Carbon. *The African Review of Physics*, 6, 0017, 143-152.

El Sayed, E.S. E. B. (2018). Natural diatomite as an effective adsorbent for heavy metals in water and wastewater treatment (a batch study). *Water Science*, *32*:32–43.

Elbedwehy, A. M., Abou-Elanwar, A. M., Ezzat, A. O., & Atta, A. M. (2019). Super effective removal of toxic metals water pollutants using multi functionalized polyacrylonitrile and Arabic gum grafts. Polymers, 11, 1938;

El-Kafrawy, A. F., El-Saeed, S. M., Farag, R. K., El-Saied, H. A-A., & Abdel-Raouf, M. E-S. (2017). Adsorbents based on natural polymers for removal of some heavy metals from aqueous solution. Egyptian Journal of Petroleum, 26: 23–32.

El-Naggar, M., E., Radwan, E., K., El-Wakeel, S., T., HanyKafafy, Gad-Allah, T., A., El-Kalliny, A., S., & Shaheen, T., I., (2018). Synthesis, characterization and adsorption properties of microcrystalline cellulose based nanogel for dyes and heavy metals removal. *International Journal of Biological Macromolecules*, 113, 248-258.

Emamjomeh, M., M., & Sivakumar, M., (2009). Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J. Environ. Manage, 90* (5), 1663–1679.

Ezeh, K., Obgu, I.C., Akpomie, K.G., Ojukwu, N.C.& Ibe, J.C. (2017). Utilizing the sorption capacity of local Nigerian sawdust for attenuation of heavy metals from solution: Isotherm, kinetic, and thermodynamic investigations. *Pacific Journal of Science and Technology*, *18*(1):251-264.

Farag, S., & Al-Afaleq, E., I. (2002). Preparation and characterization of delignified cellulose polyacrylonitrile-graft copolymer. Carbohydrate Polymers, 48(1):1-5.

Farouq, R., & Yousef, N.S. (2015). Equilibrium and kinetics studies of adsorption of copper (II) ions on natural biosorbent. *International Journal of Chemical Engineering and Applications*, 6(50), 319-324.

Feng, C., Yu, L., Xiao, Y., & An, C. (2020). Environmental Behavior and Effects of Pollutants in Water. *Journal of Chemistry*. https, Volume 2020.

Foo, K., Y., & Hameed, B., H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156 (1), 2-10.

Freundlich, H. M. F. (1906), Über die adsorption in lösungen. *Zeitschrift für Physikalische Chemie,* 57A, 385-470.

Fu, F., & Wang, Q., (2011). Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*, 92. 407-18. 10.1016/j.jenvman.2010.11.011.

Fulmer, G. R., Miller, A. J. M., Sherden, N. H., Gottlieb, H. E., Nudelman, A., Stoltz, B. M., Bercaw, J. E., & Goldberg, K. I. (2010). NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics*, 29, 2176 - 2179.

Gaber, S., Abu Haija, M., A., Priyabrata, P., Selvaraj, M., & Banat, F. (2018). Removal of Iron from Industrial Lean Methyldiethanolamine Solvent by Adsorption on Sepiolite. *Journal Separation Science and Technology*, 53 (3) , 404-416.

Gadhave, R. V., Mahanwar, P. A. & Gadekar, P. T. (2019). Effect of glutaraldehyde on thermal and mechanical properties of starch and polyvinyl alcohol blends. *Des Monomers Polym*., 23;22(1):164-170.

Ghadah, M. A. S. & Foziah, F. A. F. (2018). Adsorption study of heavy metals ions from aqueous solution by nanoparticle of wild herbs. *Egyptian Journal of Aquatic Research*, *44*:187-194.

Ghafari, M., Cui, Y., Alali, A., & Atkinson, J. D. (2019). Phenol adsorption and desorption with physically and chemically tailored porous polymers: Mechanistic variability associated with hyper-cross-linking and animation. *Journal of Hazardous Materials,* 361 (April 2018), 162-168.

Girish, C. R. (2017). Various isotherm model for multicomponent adsorption: a review. *International Journal of Civil Engineering and Technology*, 8(10), 80-86.

Girish, C. R. (2018). Simultaneous adsorption of pollutants onto the adsorbent review of interaction mechanism between the pollutants and the adsorbent. *International Journal of Engineering and Technology*, 7(4), 3613-3622.

Girish, C.R. (2017). Various isotherm models for multicomponent adsorption: a review. International Journal of Civil Engineering and Technology, 8 (10):80-86.

Gupta, A. & Balomajumder, C. (2016). Simultaneous adsorption of Cr (VI) and phenol from binary mixture using iron incorporated rice husk: Insight to multicomponent equilibrium isotherm. International Journal of Chemical Engineering, 2016:1-11.

Hala Ahmed Hegazi (2013). Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal.* 9 (3) 276-282.

Hall, K. R., Eagleton, L. C., Acrivos, A., & Vermeulen, T. (1996). Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial and Engineering Chemistry Fundamentals*, 5(2), 212-223.

Haseena M., Malik M. F., Javed A., Arshad S., Asif N., Zulfiqar S. & Hanif J. (2017). Water pollution and human health. *Environ. Risk Assess Remediat*, 1 (3), 16-19.

Hazra G. (2018). Radioactive pollution: An overview. *The Holistic Approach to Environment* 8, 2, 48-65.

He J., & Charlet L. (2013). A review of arsenic presence in China drinking water. *J Hydrol*, 492, 79-88.

Hegazi, H., A., (2013). Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*, 9(3), 276-282.

Hering, J., Missel, J. W., & Zhang, L. (2020). The rapid "teabag" method for high-end purification of membrane proteins. *Sci Rep* 10: 16167.

Hernández-Hernández, L.E., Bonilla-Petriciolet, A., Mendoza-Castillo, D. I., & Reynel-Ávila, H. E. (2017). Antagonistic binary adsorption of heavy metals using stratified bone char columns. Journal of Molecular Liquids, 241:334-346.

Hirut, G., Gebrekidan, A. & Demlie, L. (2020). Removal of heavy metals from aqueous solutions using Eucalyptus Camaldulensis: An alternate low-cost adsorbent. *Cogent Chemistry*, *6*(1):1720892.

Ho, Y. S., & McKay, F.G. (1998). Kinetic models for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. *Journal of Water Research*, 40, 11-125.

Hore, P. J. (2015). Nuclear Magnetic Resonance. *Oxford chemistry primers*, ISSN 1367-109X.

Horzum, N., Shahwan, T., Demir, M. M., & Parlak, C. Q. (2012). Synthesis of amidoximated polyacrylonitrile fibers and its application for sorption of aqueous uranyl ions under continuous flow. *Chemical Engineering Journal*, 213:41-49.

Houari, B., Louhibi, S., Tizaoui, K., Boukli-hacene, L., Benguella, B., Roisnel, T. & Dorcet, V. (2019). New synthetic material-removing heavy metals from aqueous solution and wastewater. *Arab J. Chem*. *12*(8), 5040-5048.

Hu, D., Wang, P., Li, J., & Wang, L. (2014). Functionalization of Microcrystalline Cellulose with N, N-dimethyldodecylamine for the Removal of Congo Red Dye from an Aqueous Solution. *BioResources*, 9(4),5951-5962.

Hu, Z., Pan, D., He, X., Song, D., Huang, N., Bai, Y., Xu, Y., Wang, X., Zhang, L., & Gong, F., (2014). Assessment of the MCC method to estimate sea surface currents in highly turbid coastal waters from GOCI. *International Journal of Remote Sensing*, 38(2), 572-597.

Huang, F., Xu, Y., Liao, S., Yang, D., Hsieh, L., & Wei Q. (2013). Preparation of Amidoxime Polyacrylonitrile Chelating Nanofibers and Their Application for Adsorption of Metal Ions. *Materials*, 6, 969-980.

Huang, Z., Pan, X-D., Wu, P-G., Han, J-L., & Chen, Q. (2013). Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China. *PLOS ONE* 8(9): e75007.

Ida, S. & Eva, T. (2021). Removal of Heavy Metals during Primary Treatment of Municipal Wastewater and Possibilities of Enhanced Removal: A Review. *Water*, 13, 1121.

Igberase, E. & Osifo, P. (2014). Equilibrium, kinetic, thermodynamic and desorption studies of cadmium and lead by polyaniline grafted cross-linked chitosan beads from aqueous solution. *Journal of Industrial and Engineering Chemistry*

Indah, S., Helard, D. & Binuwara A. (2017). Studies on desorption and regeneration of natural pumice for iron removal from aqueous solution. *Water Science & Technology*. *2*, 509-515.

Indah, S., Helard, D., & Binuwara, A. (2018). Studies on desorption and regeneration of natural pumice for iron removal from aqueous solution. *Water Sci Technol*, 2017 (2), 509–515.

Ismail, A., Harmuni, H., & Mohd Remy Rozainy, M., A., Z., (2017). Removal of iron and manganese using granular activated carbon and zeolite in artificial barrier of riverbank filtration. *AIP Conference Proceedings*, 1835 (1), 10.1063/1.4983796.

Istratie, R., Stoia, M., & Pa, C. (2016). Single and simultaneous adsorption of methyl orange and phenol onto magnetic iron oxide/carbon nanocomposites. *Arabian Journal of Chemistry*, 1-19.

Ivanet, A., I., Kitikova, N., V., Shashkova, I., L., Oleksiienko, O., V., Levchuk, I., & Sillanpää M., (2014). Removal of Zn^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} ions from aqueous solutions using modified phosphate dolomite. *Journal of Environmental Chemical Engineering*,2 (2), 981-987.

Ja'afar, Y., & Lawal, A., O. (2017). Studies on interference of adsorption of heavy metal ions on chelating sorbents from cassava and Amidoxime-modified Polyacrylonitrile-grafted-Cassava Starch. *Nigerian Journal of Chemical Research,* 22 (2) ,54-60.

Jamil, S. N. A. M, Daik, R. & Ahmad, I. (2007). Redox copolymerization of acrylonitrile with fumaronitrile as a precursor for carbon fibre, *Journal of Polymer Research*, 14:379-385.

Jamil, S. N. A. M., Daik, R. & Ahmad, I. (2012). Redox synthesis and thermal behavior of acrylonitrile-methyl acrylate-fumaronitrile terpolymer as precursor for carbon fiber. *International Journal of Chemical Engineering and Applications*, 3(6416-420.):

Jamshaid M., Khan A.A., Ahmed K., & Saleem M. (2018). Heavy metal in drinking water its effect on human health and its treatment techniques - a review. *International Journal of Biosciences*, 12 (4): 223-240.

Jasim, N., A., & Abdul Aziz, H., (Reviewing editor) (2020). The design for wastewater treatment plant (WWTP) with GPS X modelling, *Cogent Engineering*, 7:1.

Jin, X., Xiang, Z., Liu, Q, Chen, Y., & Lu, F. (2017). Polyethyleneimine-bacterial cellulose bioadsorbent for effective Removal of Copper and Lead Ions from Aqueous Solution. *Bioresource Technology*, 244 (Pt 1), 844-849.

Joseph, G., T., David, P., E., & Beachler, S., (1981). APTI 415: Control of Gaseous Emission.

Kabir, A., Dunlop, M., J., Acharya, B., Bissessur, R., & Ahmed, M. (2018). Polymeric Composites with Embedded Nanocrystalline Cellulose for the Removal of Iron (II) from Contaminated Water. *Polymers*,10, 1377.

Kaewtatip, K. & Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydr Polym*, 5;73(4):647-55.

Kasgoz, H., Ozbas, Z., Emine Esen, E., Sahin, C. P., & Gurdag, G. (2013). Removal of copper (II) ions with a thermoresponsive cellulose-g-poly (N-isopropyl acrylamide) copolymer. *Journal of Applied Polymer Science*, 130 (6): 4440-4448.

Kaveeshwar, A., R., Ponnusamy, S., K., Revellame, E., D., Gang, D., D., Zappi, M., E. & Subramaniam, R. (2018). Pecan Shell Based Activated Carbon for Removal of Iron (II) from Fracking Wastewater: Adsorption kinetics, isotherm and thermodynamic studies. *Process Safety and Environmental Protection*, 114: 10-122.

Khullar, R. (2008). Grafting of acrylonitrile onto cellulosic material derived from bamboo (Dendrocalamus strictus). *eXPRESS Polymer Letters,* 2(1):12-18.

Kiani, G., R., Sheikhloie, H. & Arsalani, N., (2011). Heavy metal ion removal from aqueous solutions by functionalized polyacrylonitrile. *Desalination*, 269, 266–270.

Kim, T., Kim, T., K., & Zoh, K., D., (2020). Removal mechanism of heavy metal (Cu, Ni, Zn, and Cr) in the presence of cyanide during electrocoagulation using Fe and Al electrodes. *Journal of Water Process Engineering*,33,101109.

Kinuthia G.K, Ngure V., Beti D., Lugalia R. Wangila A. & Kamau L. (2020). *Scientific Reports*,10:8434.

Kipcak A. S., Ismail Q., Doymaz I., & Piskin S. (2014). Modeling and investigation of the swelling kinetics of acrylamide-sodium acrylate hydrogel. Journal of Chemistry, 281063.

Kivenson V., Lemkau K. L., Pizarro O., Yoerger D. R., Kaiser C., Nelson R. K., Carmichael C., Paul B. G., Reddy C. M. & Valentine D. L. (2019). Ocean dumping of containerized DDT waste was a sloppy process. *Environ. Sci. Technol*., 53, 6, 2971-2980.

Klemm, D., Heublein, B., Fink, H., P., & Bohn, A., (2005). Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed Engl*, 44(22):3358-93.

Kovacova, Z., Demcak, S., & Balintova, M., (2019). Removal of Copper from Water Solutions by Adsorption on Spruce Sawdust. *Proceedings, 16*, 52.

Kragovića, M., Stojmenovića, M., Petrovićb, J., Loredoc, J., Pašalića, S., Nedeljkovićd, A. & Ivica Ristovićd, I. (2019). Influence of Alginate Encapsulation on Point of Zero Charge (pHpzc) and Thermodynamic Properties of the Natural and Fe (III) -Modified Zeolite. *Procedia Manufacturing*, 32, 286-293.

Kumar, D., Pandey, J., Raj, V. & Kumar, P. (2017). A Review on the Modification of Polysaccharide Through Graft Copolymerization for Various Potential Applications. *The Open Medicinal Chemistry Journal*, 11:109-126.

Kumar, N., Kumar A, Marwein B. M., Verma D. K., Jayabalan I., Kumar A., & Ramamoorthy D. (2021). Agricultural activities causing water pollution and its mitigation- A review. International Journal of Modern Agriculture, 10 (1), 590-609.

Kumar, M., Dosanjh, H. S. & Singh, H. (2018). Removal of lead and copper metal ions in single and binary systems using biopolymer modified spinel ferrite. Journal of Environmental Chemical Engineering, 6: 6194–6206.

Kumar, V., Naithani, S., & Pandey, D., (2011). Optimization of reaction conditions for grafting of α-cellulose isolated from Lantana camara with acrylamide. *Carbohydrate Polymers*, 86, 760-768.

Kwon, T. N. & Jeon, C. (2012). Desorption and regeneration characteristics for previously adsorbed indium ions to phosphorylated sawdust. *Environmental Engineering Research*, *17* (2), 65–67.

Laabd, M., Chafai, H., Essekri, A., Elamine, M., Al-muhtaseb, S.A., Lakhmiri, R., & Albourine, A. (2017). Single and multi-component adsorption of aromatic acids using an eco-friendly polyaniline-based biocomposite. Sustain. Mater. Technol., 12, 35–43.

Lagergren, S. (1898), Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskaps-Akademiens. Handlingar, Band 24, Section II, No.4, 1-39.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40, 1361-1403.

Lata, S., Singh, P. K., & Samadder, S. R. (2015). Regeneration of adsorbents and recovery of heavy metals: a review. *Int. J. Environ. Sci. Technol*, 12:1461–1478.

Layth Mohammed, M. N. M. Ansari, Grace Pua, Mohammad Jawaid, M. & Saiful Islam, S. (2015). "A Review on Natural Fiber Reinforced Polymer Composite and Its Applications", *International Journal of Polymer Science*, vol. 2015, Article ID 243947, 15 pages, 2015.

Leitão, A., & Serrão, R. (2005). Adsorption of phenolic compounds from water on activated carbon: Prediction of multicomponent equilibrium isotherms using single-component data. *Adsorption*, 11 (2 SPEC. ISS.), 167-179.

León, M., Silva, J., Carrasco S., & Barrientos, N. (2020). Design, Cost Estimation and Sensitivity Analysis for a Production Process of Activated Carbon from Waste Nutshells by Physical Activation. *Processes*. 8 (8): 945.

Li, T., Y. Liu, Q. Peng, X. Hua, T. Liao & H. Wanga. (2013). Removal of lead (II) from aqueous solution with ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles: Kinetic and equilibrium modeling. *Chem. Eng. J. 214*, 189–197.

Lim, S. F. & Agnes Lee, Y. W. (2015). Kinetic study on removal of heavy metal ions from aqueous solution by using soil. *Environ. Sci Pollut Res., 22*, 10144–10158.

Lin, L., Xu, X., Papelis, C. & Xu, P. (2017). Innovative use of drinking water treatment solids for heavy metals removal from desalination concentrate: Synergistic effect of salts and natural organic matter. *Chemical Engineering Research and Design*, 120; 231-239.

Lin, Y., Chen, H., Lin, K., Chen, B. & Chiou, C. (2011). Application of Magnetic particles modified with amino group to remove copper ions from aqueous solution. *J. Environ. Sci*., *23*, 44–50. doi: 10.1016/S1001-0742(10)60371-3.

Liu, C., Liang, X., Liu, J. & Yuan, W. (2015). Desorption of copper ions from the polyamine functionalized adsorbents: Behaviour and mechanism. *Adsorpt. Sci. Technol*. 34:455–468.

Liu, C-F., Ren, J-L., Xu, F., Liu, J-J., Sun, J-X., & Sun, R-C. (2006). Isolation and Characterization of Cellulose Obtained from Ultrasonic Irradiated Sugarcane Bagasse. *Journal of Agricultural and Food Chemistry*, 54(16):5742-8.

Liu, Q., Li, Y., Chen, H., Lu, J., Yu, G., Möslang, M.& Zhoua, Y. (2020). Superior adsorption capacity of functionalised straw adsorbent for dyes and heavy-metal ions. Journal of Hazardous Materials, 382, 121040.

Liu, X., Chen, H., Wang, C., Qu, R., Ji, C., Sun, C. & Zhang, Y. (2010). Synthesis of porous acrylonitrile/methyl acrylate copolymer beads by suspended emulsion polymerization and their adsorption properties after amidoximation. *Journal of Hazardous Materials*, 175:1014-1021.

Liu, X., Chen, H., Wang, C., Qu, R., Ji, C., Sun, C., & Zhang, Y. (2010). Synthesis of porous acrylonitrile/methyl acrylate copolymer beads by suspended emulsion polymerization and their adsorption properties after amidoximation. *Journal of Hazardous Materials*, 175: 1014-1021.

Lopera-Valle, A. & Elias, A., (2019). Amine Responsive Poly (lactic acid) (PLA) and Succinic Anhydride (SAh) Graft-Polymer: Synthesis and Characterization. *Polymers*, 11, 1466.

Lutfor, M. R., Rohani, N., Mustapa, N., & Yusoff, M. (2014). Synthesis of Polyamidoxime Chelating Ligand from Polymer-Grafted Corn-Cob Cellulose for Metal Extraction. *Journal of Applied Polymer Science*, 131(19): n/a-n/a.

Lutfor, M., R, Silong, S., Haron, J., Rahman, M., Z., A. & Ahmad, M. (2003). Modification of sago starch by graft copolymerization. Effect of reaction conditions on grafting parameters. *International Journal of Polymeric Materials*, 52(3):189-201.

Mahmood, M., BrbootI Balasim, A., AbiD, & Al-ShuwaikI, N., M., (2011). Removal of Heavy Metals Using Chemicals Precipitation. *Eng & Tech Journal*, 29 (3), 595-612.

Mai-Prochnow, A., Clauson, M., & Hong, J. (2016). Gram positive and Gram negative bacteria differ in their sensitivity to cold plasma. *Sci Rep* 6,38610.

Manyangadze, M., Chikuruwo, N.H.M., Narsaiah, T. B., Chakra, C. S., Radhakumari, M., & Danha, G. (2020). Enhancing adsorption capacity of nano-adsorbents via surface modification: A review. *South African Journal of Chemical Engineering*, 31 :25-32.

Masry, B., A, El-Din, A., M., S, & Al-Aidy, H., A. (2021) Ceric-ions redox initiating technique for Zirconium and Niobium separation through graft copolymerization of natural polysaccharides, *Separation Science and Technology*.

McKay, G. & Al Duri, B. (1987). Simplified model for the equilibrium adsorption of dyes from mixtures using activated carbon. *Chemical Engineering and Processing: Process Intensification*, 22(3), 145-156.

Medellin-castillo, N. A., Padilla-ortega, E., Regules-martinez, M. C. & Carranza-alvarez, C. (2017). Single and competitive adsorption of Cd (II) and Pb (II) ions from aqueous solutions onto industrial chili seeds (Capsicum annuum) waste. Sustainable Environmental Research, 2017:1-9.

Mia R, Selim M. & Shamim AM. (2019). Review on various types of pollution problem in textile dyeing and printing industries of Bangladesh and recommendation for mitigation. *J. Textile Eng. Fashion Technol*, 5 (4), 220-226.

Millero, F. (2001). Speciation of metals in natural waters. *Geochemical Transactions*, 2, Article number 57.

Mishra, A., Sharma, S., & Gupta, B. (2011). Studies on the amidoximation of polyacrylonitrile films: Influence of synthesis conditions. *Journal of Applied Polymer Science,* 121, 2705-2709.

Mohamed H. El-Newehy a,b,*, Abdullah Alamri a, Salem S. Al-Deyab (2014). Optimization of amine- terminated polyacrylonitrile synthesis and characterization. *Arabian Journal of Chemistry*, 7, 235–241.

Mohammadnezhad, G., Dinari, M., & Soltani, R. (2016). The preparation of modified boehmite/PMMA nanocomposite by in-situ polymerization and assessment of their capability for copper removal. *N. J. Chem*., *40*, 3612–3621.

Mohammadnezhad, G., Soltani, R., Abad, S., & Dinaro, M. (2017). A novel porous nanocomposite of animated silica MCM-41 and Nylon-6: Isotherm, kinetic and thermodynamic studies on adsorption of Cu (II) and Cd (II) *J. Appl. Polym. Sci*., *134*, 45383.

Mohib U., Ruqia N., Muslim K., Waliullah, K., Mohib, S., Sahib, G. A & Amir, Z. (2020). The effective removal of heavy metals from water by activated carbon adsorbents of Albizia lebbeck and Melia azedarach seed shells. *Soil and Water Research, 15*(1), 30–37.

Moradi, O., Mirza, B., Norouzi, M., & Fakhri, A. (2012). Removal of Co (II), Cu (II) and Pb (II) ions by polymer based 2-hydroxyethyl methacrylate: Thermodynamics and desorption studies. *J. Environ. Health Sci. Eng., 9*, 31–33.

Mostafa R., Hossein, A. & Hamed, B. (2020). Thermodynamic study of iron (III) removing by thesynthesizeda-alumina powder and evaluating thecorresponding adsorption isotherm models using response surface method. *Arabian Journal of Chemistry*, *13*, 4254-4262.

Mulu, B. D. (2013). Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (Eragrostis Tef) agricultural waste. *Journal of Thermodynamics. Volume 2013*, Article ID 375830.

Mungathia, T., Thumbi, G. M. & Mwangi, J. K. (2013). Extended Langmuir Model Fitting to The Filter Column Adsorption Data of Copper and Zinc. *Journal of Agriculture, Science and Technology*, 15(1): 192-214.

Mustafa S. K. & AlSharif M. A. (2018). Copper (Cu) an Essential Redox-Active Transition Metal in Living System—A Review Article. *American Journal of Analytical Chemistry*, 19 (1): 15-26.

Myalowenkosi, I., Sabella, Kunene, K., Kanchi, S., Xhakaza, N. M., Bathinapatla, A., Mdluli, P., Sharma, D. & Bisetty, K. (2019). Removal of copper (II) from wastewater using green vegetable waste derived activated carbon:An approach to equilibrium and kinetic study. Arabian Journal of Chemistry,12, 4331–4339.

Mzinyane, N. N., Ofomaja, A. E., & Naidoo, E. B. (2021). Synthesis of poly (hydroxamic acid) ligand for removal of Cu (II) and Fe (II) ions in a single component aqueous solution. *South African Journal of Chemical Engineering*, 35, 137-152.

Nair, S., B., & Jyothi, A., N. (2014). Cassava Starch-graft-Polymethacrylamide Copolymers as Flocculants and Textile Sizing Agents. *Journal of Applied Polymer Science*, 131(2).

Narges, S. L., Zhaleh, F. & Aliakbar, D. K. (2018). Optimization of adsorption parameters for Fe (III) ions removal from aqueous solutions by transition metal oxide nanocomposite. *Green Chemistry Letters and Reviews*, *11*(4):404-413,

Naser Samadi, Reza Ansari, & Bakhtiar Khodavirdilo (2017). Removal of Copper ions from aqueous solutions using polymer derivations of poly (styrene-altmaleic anhydride). *Egyptian Journal of Petroleum,* 26, 375–389.

Navarro, D., Abelilla, J. J., & Stein, H. H. (2019). Structures and characteristics of carbohydrates in diets fed to pigs: a review. *Journal of animal science and biotechnology*, 10, 39.

Ndi Nsami, J., & Mbadcam, J., K., (2013). The Adsorption Efficiency of Chemically Prepared Activated Carbon from Cola Nut Shells by on Methylene Blue. *Journal of Chemistry.* Volume 2013, Article ID 469170, 7 pages.

Nethaji, S., Sivasamy, A. & Mandal, A. (2012). Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *Int. J. Environ*., *10*: 231-42.

Ngah, W. S. W., Ab Ghani, S. & Kamari, A. (2005). Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresource Technology*, *96*(4): 443–450.

Niu, X., Zheng, L., Zhou, J., Dang, Z. & Li, Z. (2014). Synthesis of an adsorbent from sugarcane bagass by graft copolymerization and its utilization to remove Cd (II) ions from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, *45* :2557-2564.

Njikam, E., & Schiewer, S. 2012. Optimization and kinetic modeling of cadmium desorption from citrus peels: a process for biosorbent regeneration. *Journal of Hazardous Materials*, 213–214 (1), 242–248.

Noruzi, E., B., Shaabani, B., Geremia, S., Hickey, N., Nitti, P., & Kafil, H., S. (2020). Synthesis, Crystal Structure, and Biological Activity of a Multidentate Calix [4] arene Ligand Doubly Functionalized by 2-Hydroxybenzeledene-Thiosemicarbazone. *Molecules*, 25(2): 370.

Nugroho R. W., Odelius K., Höglund A., & Albertsson C. (2016). Highlighting the importanc of surface grafting in combination with layer-by-layer approach for fabricating advanced 3D poly(I-lactide) microsphere scaffolds. *Chemistry of Materials*, 28 (10), 3298-3307.

Ocreto, J., Go, C. I., Chua, J. C., Apacible, C. J. & Vilando, A. (2019). Competitive effects for the adsorption of copper, cadmium and lead ions using modified activated carbon from bamboo. MATEC Web of Conferences 268, 06021.

Ohwoavworhua, F., O., & Adelakun, T., A., (2010). Non-wood Fibre Production of Microcrystalline Cellulose from Sorghum caudatum: Characterisation and Tableting Properties. *Indian J Pharm Sci*, 72(3):295-301.

Olds H. T., Corsi S. R., Dila D. K., Halmo K. M. & Bootsma M. J. (2018). High levels of sewage contamination released from urban areas after storm events: A quantitative survey with sewage specific bacterial indicators. *PLOS Medicine*, 15 (7): e1002614.

Palani G., Arputhalatha A., Kannan K., Lakkaboyana S.K., Hanafiah M.M., Kumar V., Marella K. (2021) Current Trends in the Application of Nanomaterials for the Removal of Pollutants from Industrial Wastewater Treatment-A Review. *Molecules,* 26 ,2799.

Parmar, M., & Thakur, L., S., (2013). Heavy metal Cu, Ni and Zn: Toxicity, Health Hazards and Their Removal Techniques by Low Cost Adsorbents: A Short Overview. *International Journal of Plant, Animal and Environmental Sciences*, 3 (3) 143-157.

Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review. *Appl Water Sci, 9*, 45.

Pathania, D., Thakura, M., Sharma, G., & Mishra, A. K. (2018). Tin (IV) phosphate/poly(gelatin-cl-alginate) nanocomposite: Photocatalysis and fabrication of potentiometric sensor for Pb (II). *Materials Today Communication*, 14: 282-293.

Paul D. (2017). Research on heavy metal pollution of river Ganga: A review. *Annals of Agrarian Science,* 15(2):278-286

Pavia, D. L., Lampman, G. M. & Kriz, G. S. (2001). Introduction to spectroscopy: A Guide for student of organic chemistry. Third Edition. BROOKS/COLE, ISBN:0-03-031961-7.

Petrovic, B., Gorbounov, M., & Soltani, S., M. (2021). Influence of surface modification on selective CO_2 adsorption: A technical review on mechanisms and methods. *Microporous and Mesoporous Materials,* 312 ,11075.

Piotrowski, S., & Carus, M., (2011). Multi-criteria evaluation of lignocellulosic niche crops for use in biorefinery processes. nova-Institut GmbH, Hürth, Germany. 26 pages.

Pohl, A. (2020). Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. *Water Air Soil Pollut* , 231, 503.

Pourjavadi, A. & Kurdtabar, M. (2009). Effect of different bases and neutralization steps on porosity and properties of collagen-based hydrogels. *Polymer International*, 59 (1): 36-42.

Preisner, M. (2020). Surface Water Pollution by Untreated Municipal Wastewater Discharge Due to a Sewer Failure. *Environ. Process*, 7, 767–780.

Putro, J. N., Santoso, S. P., Ismadji, S. & Ju, Y-H. (2017). Investigation of heavy metal adsorption in binary system by nanocrystalline cellulose-Bentonite nanocomposite: Improvement on extended Langmuir isotherm model. Microporous and Mesoporous Materials, 246:166-177.

Qian, G., Li, M., Wang, F., & Liu, X., (2014). Removal of Fe^{3+} from Aqueous Solution by Natural Apatite. *Journal of Surface Engineered Materials and Advanced Technology*, 4, 14-20.

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W. & Zhang, Q. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University Science A*., 10(5), 716-724.

Rahman, M. O., Rahman, N., Foysal Ahmed, G. M., Sajid Hasan, M., Dafader, N. C., Jahangir Alam, Sultana, S., & Ahmed, F.T. (2020). Synthesis and implication of grafted polymeric adsorbent for heavy metal removal. *SN Applied Sciences*, *2*, 1089.

Rahman, M., L., Sarkar, S., M., Farid, E., M., Arshad, S., E., Sarjadi, M., S., & Wid, N., (2018). Synthesis of Tapioca Cellulose-based Poly(amidoxime) Ligand for Removal of Heavy Metal Ions. *Journal of Macromolecular Science*, 57 (2):83-99.

Rahman, M., L., Yusoff, M., Fazli, M., & Abu Samah, N. (2014). Synthesis of polymeric chelating ligands from sago starch for metal removal from electroplating wastewater. *Indian Journal of Chemical Technology*, 21(1):30-37.

Rahman, N., Sato, N., Yoishioka, S., Sugiyama, M., Okebe, H., & Hara, K. (2013). Selective Cu (II) adsorption from aqueous solution including Cu (II), Co (II) and Ni (II) by modified acrylic acid grafted PET (polyethylene terephthalate film) *Polym. Sci*., *2013*, Article ID 536314.

Rai, M. K., Shahi, G., Meena, V., Meena, R., Chakraborty, S., Singh, R.S., & Rai, B.N. (2016). Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4. *Resource-Efficient Technologies*, *2*, S63–S70.

Ramesh, S. T., Rameshbabu, N., Gandhimathi, R., Nidheesh, P. V., & Srikanth Kumar, M. (2012). Kinetics and equilibrium studies for the removal of heavy metals in both single and binary systems using hydroxyapatite. Appl Water Sci., 2, 187–197.

Ramesh, S., T., Rameshbabu, N., Gandhimathi, R., Nidheesh, P.V. & Kumar, M. S. (2012). Kinetics and equilibrium studies for the removal of heavy metals in both single and binary systems using hydroxyapatite. *Applied Water Science*, 2, 187–197.

Rangabhashiyam, S., Anu, N., Giri, M. S. N. & Selvaraju, N. (2014). Relevance of isotherm models in biosorption of pollutants by agricultural by-products. J. Environ. Chem. Eng., 2 :398–414.

Rania, F. & Yousef, N. S. (2015). Equilibrium and kinetics studies of adsorption of copper (II) ions on natural biosorbent. *International Journal of Chemical Engineering and Applications. 6* (5), 319-324.

Renu, Agarwal, M., & Singh, K., (2017). Heavy metal removal from wastewater using various adsorbents: a review. *Journal of Water Reuse and Desalination*, 7 (4): 387-419.

Repo, E., Warchol, J., K., Bhatnagar, A., & Sillanpaa, M., (2011). Heavy metals adsorption by novel EDTA-modified chitosan-silica hybrid materials. *J. Colloid Interface Sci*., 358 (1), 261-267.

Rey, P. A., & Varsanik, R. G. (1986). Application and Function of Synthetic Polymeric Flocculents in Wastewater Treatment. *Advances in Chemistry*, Vol. 213. ISBN13: 9780841209312.

Ropa, K., Mbui, D., Njomo, N., Karuku, G. N., Michira, I. & Ajayi, R. F. (2019). Biodegradable water hyacinth cellulose-graft-poly(ammonium acrylate-co-acrylic acid) polymer hydrogel for potential agricultural application. *Heliyon,* 5(3), e01416.

Rudi N.N, Muhamad M.S, Chuan L.T, Alipal J., Omar S., Hamidon N., Abdul Hamid N.H, Mohamed Sunar N., Ali R, & Harun H. (2020). Evolution of adsorption process for manganese removal in water via agricultural waste adsorbents. *Heliyon*, 6, e05049.

Saeed, K., Haider, S., Oh, T-J., & Parka, S-Y. (2008). Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption. *Journal of Membrane Science,* 322 (2): 400-405.

Saleem, J., Shahid, U., Hijab, M., Mackey, H. & McKay, G. (2019). Production and applications of activated carbons as adsorbents from olive stones. *Biomass Conversion and Biorefinery,* 9,775–802.

Salimnezhad A., Soltani-Jigheh H., & Soorki AA. (2020). Effects of oil contamination and bioremediation on geotechnical properties of highly plastic clayey soil. Journal of Rock Mechanics and Geotechnical Engineering,

Salmani, M., H., Ehrampoush, M., H., Sheikhalishahi, S., & Dehvari, M., (2012). Removing Copper from Contaminated Water Using Activated Carbon Sorbent by Continuous Flow. *Journal of Health Researches*, 1(1): 11-18.

Samadi, N., Ansari, R. & Khodavirdilo, B. (2017). Removal of Copper ions from aqueous solutions using polymer derivations of poly (styrene-altmaleic anhydride). Egyptian Journal of Petroleum, 26: 375–389.

Saputra, A., Qadhayna, L. & Pitaloka, A. (2014). Synthesis and Characterization of Carboxymethyl Cellulose (CMC) from Water Hyacinth Using Ethanol-Isobutyl Alcohol Mixture as the Solvents. *International Journal of Chemical Engineering and Applications*, 5(1):36-40.

Sdiri, A. T., Higashi, T., & Jamoussi, F. (2014). Adsorption of copper and zinc onto natural clay in single and binary systems. *International Journal of Environmental Science and Technology,* 11(4), 1081-1092.

Selvi A, Rajasekar A, Theerthagiri J, Ananthaselvam A, Sathishkumar K, Madhavan J and Rahman PKSM. (2019). Integrated Remediation Processes Toward Heavy Metal Removal/Recovery from Various Environments-A Review. *Front. Environ, Sci*. 7:66.

Sepehr, M. N., Amrane, A., Karimaian, K. A., Zarrabi, M. & Ghaffari, H. R. (2014). Potential of waste pumice and surface modified pumice for hexavalent chromium removal: Characterization, equilibrium, thermodynamic and kinetic study. *Journal of the Taiwan Institute of Chemical Engineers, 45*(2), 635-647.

Sepehr, M., N., Amrane, A., Karimaian, K., A., Zarrabi, M., & Ghaffari, H., R. (2014). Potential of waste pumice and surface modified pumice for hexavalent chromium removal: Characterization, equilibrium, thermodynamic and kinetic study. *Journal of the Taiwan Institute of Chemical Engineers*, 45 (2), 635-647.

Shaaban, A., F., Fadel, D., A., Mahmoud, A., A., Elkony, M., A., & Elbahy, S., M. (2014). Synthesis of a new chelating resin bearing amidoxime group for adsorption Cu (II), Ni (II) and Pb (II) by batch and fixed-bed column methods. *Journal of Environmental Chemical Engineering*, 2, 632-641.

Shahbeig, H., Bagheri, N., Ghorbanian, S. A., Ahmad, H., & Poorkarimi, S. (2013). A new adsorption isotherm model of aqueous solutions on granular activated carbon. *World Journal of Modelling and Simulation*, 9(4), 243-254.

Shanthi T. & Selvarajab V.M. (2012). Removal of Cr (VI) and Cu (II) Ions from aqueous solution by carbon prepared from Henna leaves. *Journal of Chemistry*, 2013, Article ID 304970.

Sharma G., Pathania D. & Naushad M. (2015). Preparation, characterization, and ion exchange behavior of nanocomposite polyaniline zirconium (IV) selenotungs to phosphate for the separation of toxic metal ions. *Ionics*, *21*,1045–1055.

Sharma, K., Vyas, R. K., Singh, K., & Dalai, A. K. (2018). Degradation of a synthetic binary dye mixture using reactive adsorption: Experimental and modeling studies. *Journal of Environmental Chemical Engineering*, 6(August), 5732-5743.

Shavandi, M. A., Haddadian, Z., Ismail, M.H.S., Abdullah, N. & Abidin, Z.Z. (2012) Removal of Fe (III), Mn (II) and Zn (II) from palm oil mill effluent (POME) by natural zeolite. *J. Taiwan Inst. Chem. Eng.*, *43*, 750–759.

Shirvanimoghaddam, K., Hamim, S., U., Akbari, M., K., Fakhrhoseini, S., M., Khayyam, H., Pakseresht, A., H., Ghasali, E., Mahla Zabet, M., Munir, K., S., Jia, S., Davim, J., P., & Naebe, M., (2017). Carbon fiber reinforced metal matrix composites: Fabrication processes and properties. *Composites, Part A* 92, 70–96.

Singha, A., S., & Guleria, A., (2015). Synthesis and Applications of Functional Polymers from Natural Okra Fibers for Removal of Cu (II) Ions from Aqueous Solution, *Journal of Natural Fibers*, 12:6, 587-603.

Sinha, P., Datar, A., Jeong, C., Deng, X., Chung, Y. G., & Lin, L-C. (2019). Surface Area Determination of Porous Materials Using the Brunauer–Emmett–Teller (BET) Method: Limitations and Improvements. *The Journal of Physical Chemistry C*, 123 (33), 20195-20209

Sizirici, B., Yildiz, I., Alyammahi, A., Obaidalla, F., Almehairbi, M., & Alkhajeh, S. (2018). Adsorptive removal capacity of gravel for metal cations in the absence/presence competitive adsorption. *Environmental Science and Pollution Research*, *25*, 7530-7540.

Soliman, E. A., Mansour, E-S. M. E-S, Hassan, H. A. M., & Hassan, N. A. M. (2014). Optimization of Graft Polymerization and Performance of Carboxymethyl Chitosan / Polyacrylamide Flocculants. *Journal of Research & Developments in Chemistry*, Vol. 2014 (2014), Article ID 351498.

Song, C., Wu, S., Cheng, M., Tao, P., Shao, M. & Gao, G. (2014). Adsorption studies of coconut shell carbons prepared by KOH activation for removal of lead (II) from aqueous solutions. *Sustainability*, *6*, 86-98.

Sruthi, P. R. & Anas, S. (2020). An overview of synthetic modification of nitrile group in polymers and applications. *Journal of Polymer Science*, 58 (8), 1039-1061.

Sruthi, P., R. & Anas, S. (2020). An overview of synthetic modification of nitrile group in polymers and applications. *J.Polym.Sci*, 58, 1039–1061.

Subri, N., N., S., Jamil, S., S., A., Peter, A., G., Cormack, Abdullah, L., C., Kamaruzaman, S., & Adeyi, A., A., (2020). The synthesis and characterisation of porous and monodisperse, chemically modified hypercrosslinked poly(acrylonitrile)-based terpolymer as a sorbent for the adsorption of acidic pharmaceuticals. *e-Polymers*, 20,328–345.

Tan, K., Ma, W., Wu, F. & Du, Q. (2019). Random forest–based estimation of heavy metal concentration in agricultural soils with hyperspectral sensor data. *Environmental Monitoring and Assessment,* 191, 446.

Tan, XM. & Rodrigue, D. (2019). A Review on Porous Polymeric Membrane Preparation. Part I: Production Techniques with Polysulfone and Poly (Vinylidene Fluoride). *Polymers*, 11, 1160.

Taylor, T. A, & Chandrashekhar G. Unakal, C. G. (2021). Staphylococcus Aureus. StatPearls Publishing LLC. Bookshelf ID: NBK441868PMID: 28722898.

Terdputtakun, A., Arqueropanyo, Oa., & Sooksamiti, P. (2017). Adsorption isotherm models and error analysis for single and binary adsorption of Cd (II) and Zn (II) using leonardite as adsorbent. Environ Earth Sci, 7.6, 777.

Terdputtakun, A., Arqueropanyo, O-A., Sooksamiti, P., Janhom, S. & Naksata, W. (2017). Adsorption isotherm models and error analysis for single and binary adsorption of Cd (II) and Zn (II) using leonardite as adsorbent. Environmental Earth Sciences, 76, 777.

Thoorens, G., Krier, F., Leclercq, B., Carlin, B., & Evrard, B., (2014). Microcrystalline cellulose, a direct compression binder in a quality by design environment--a review. *Int J Pharm*., 473 (1-2) :64-72.

Tosh B. & Routray C. R. (2014). Grafting of cellulose based materials: a review. *Chemical Science Review and Letters.* 3 (10), 74 -92.

Tran, H., N., and Chao, H., P., (2018) Adsorption and desorption of potentially toxic metals on modified biosorbents through new green grafting process. *Environ. Sci. Pollut., 25*, 12808–12820.Volume 2013, Article ID 469170, 7 pages.

Tsibranska, I. & Hristova, E. (2011). Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones. *Bulgarian Chemical Communications*, 43(3):370-377.

Uddin, M., K., (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*, (308), 438-462.

Uddin, M., T., Islam, M., A., Mahmud, S., & Rukanuzzaman, M., (2009). Adsorptive removal of methylene blue by tea waste. *J. Hazard. Mater*, 164 (2009), 53-60.

Ulucan-Altuntas, K. E., Debik, I. I. & Yoruk, D. Kozal (2017). Single and binary adsorption of copper and nickel metal ions on nano zero valent iron (nZVI): A kinetic approach. Desalination and Water Treatment, 93, 274–279.

United Nations World Water Development Report 2019. Retrieved on 2 June 2021.

United Nations World Water Development Report 2021. Retrieved on 2 June 2021.

Uzunova, S., Uzunov, I. & Angelova, D. (2013). Liquid-phase sorption of oil by carbonized rice husks: impact of grain size distribution on the sorption kinetics. *Journal of Chemical Technology and Metallurgy*, 48(5), 505-512.

Varesano, C., Vineis, A., Aluigi & Rombaldoni, F. (2011). Antimicrobial polymers for textile products. In Science against Microbial Pathogens: Communicating Current Research and Technological Advances, *Formatex*, 99-110.

Viera-Herrera, C., Santamaría-Aguirre, J., Vizuete, K., Debut, A., Whitehead, D., C. & Alexis, F. (2020). Microcrystalline Cellulose Extracted from Native Plants as an Excipient for Solid Dosage Formulations in Drug Delivery. *Nanomaterials*, 10, 975.

Vinodhini, P., A., & Sudha, P., N., (2017). Removal of heavy metal chromium from tannery effluent using ultrafiltration membrane. *Springer: Textiles and Clothing Sustainability*,2: 5.

Wagmer, J. L. (1967). Selective adsorption process. U.S. Patent No 3 430 418A. March 4, 1967.

Wan, Z., Xiong, Z., Ren, H., Huang, Y., Liu, H., Xiong, H., & Han, J. (2011). Graft copolymerization of methyl methacrylate onto bamboo cellulose under microwave irradiation. *Journal of Carbohydrate Polymers*, 83 (1), 264-269.

Wang, F., Pan, Y., Cai, P., Guo, T., & Xiao, H. (2017). Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. Bioresource Technology, 241:482–490.

Wankasi, D., Horsfall Jnr, M. & Spiff, AL. (2005). Desorption of Pb^{2+} and Cu^{2+} from Nipa palm (Nypa fruticans Wurmb) biomass. *African Journal of Biotechnology*, 4 (9): 923-927

Wankasi, D., Horsfall M., J., & Spiff, A., I. (2005). Desorption of Pb^{2+} and Cu^{2+} from Nipa palm (Nypa fruticans Wumb) biomass. *African Journal of Biotechnology*, 4 (9), 923–927.

Webb, A. (2016). CHAPTER 1: The Principles of Magnetic Resonance, and Associated Hardware, in Magnetic Resonance Technology: Hardware and System Component Design, 2016, pp. 1-47 DOI: 10.1039/9781782623878-00001, eISBN: 978-1-78262-387-8, From Book Series: New Developments in NMR.

Weber, Jr., J.W. & Morris, J.C. (1963). Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division-ASCE*, *89*(2), 31-59.

Wu, F.C., Tseng, R. L., & Juang, R. S. (2009). Initial behavior of interparticle diffusion model used in the description of adsorption kinetics. *Chemical Engineering Journal, 153*(1-3), 1-8.

Wu, N. & Li, Z. (2013). Synthesis and characterization of poly (HEA/MALA) hydrogel and its application in removal of heavy metal ions from water. *Chemical Engineering Journal*, 215-216: 894-902.

Yang, S., Wu, Y., Aierken, A., Zhang, M., Fang, P., & Fan, Y. (2016). Mono/competitive adsorption of Arsenic (III) and Nickel (II) using modified green tea waste. Journal of the Taiwan Institute of Chemical Engineers, 60, 213-222.

Younas, F., Mustafa, A., Farooqi, Z., U., R., Wang, X., Younas, S., Mohy-Ud-Din, W., Ashir Hameed, M., Mohsin Abrar, M., Maitlo, A., A., & Noreen, S. (2021). Current and Emerging Adsorbent Technologies for Wastewater Treatment: Trends, Limitations, and Environmental Implications. *Water*, 13, 215.

Yousef, R., Qiblawey, H. & El-Naas, M., H. (2020). Adsorption as a Process for Produced Water Treatment: A Review. *Processes*, 8, 1657; doi:10.3390/pr8121657.

Yu, B., Zhang, Y., Shukla, A., Shukla, S.S. & Dorris, K.L., (2000). The removal of heavy metal from aqueous solutions by sawdust adsorption - RemovalAnya of copper. *J. Hazard. Mater. 80*(1), 33–42.

Yuanan Hu &Xueping Liu &Jinmei Bai &Kaimin Shih &Eddy Y. Zeng &Hefa Cheng (2013). Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization. *Environ Sci Pollut Res* 20:6150–6159.

Yue, R., Chen, Q., Li, S., Zhang, X., Huang, Y. & Feng, P. (2018). One-step synthesis of 1,6-hexanediamine modified magnetic chitosan microspheres for fast and efficient removal of toxic hexavalent chromium. *Sci. Rep.*, *8*, 11024.

Yussuf, N., M., Embong, Z., Abdullah, S., Masirin, M., I., M., Tajudin, S., A., A., S. Ahmad, S., Sahari, S., K., Anuar, A., A., & Maxwell, O., (2018). The enhancement of heavy metal removal from polluted river water treatment by integrated carbon-aluminium electrodes using electrochemical method. *IOP Conf. Series: Materials Science and Engineering,* 298.

Zafra-Mejía, C. A., Alarcón-Hincapiè J. C., & Gutièrrez-Malaxechebarría A. M. (2020). Cost/Benefit Analysis for the Use of Different Coagulants in a Drinking Water Treatment Plant. *International Journal of Advanced Science and Technology*, 29 (4) 8547-8555.

Zahri N.A.M, Jamil Md. S.N.A, Abdullah L. C., Choong S. Y. T., Mobarekeh M.N, Sim J.H. & Rapeia N.S.M. (2015). Improved Method for Preparation of Amidoxime Modified Poly(acrylonitrile-co-acrylic acid): Characterizations and Adsorption Case Study. *Polymers*,7(7),1205-1220.

Zaini, M. A. A., Amano, Y., & Machida, M. (2010). Adsorption of Heavy Metals onto Activated Carbons Derived from Polyacrylonitrile Fiber. *Journal of Hazardous Materials*, 180(1-3):552-60

Zakaria, Z., Zulkafflee, N., S., Mohd Redzuan N., A., Selamat, J., Ismail, M., R., Praveena S., M., Tóth, G., & Abdull Razis, A., F. (2021). Understanding Potential Heavy Metal Contamination, Absorption, Translocation and Accumulation in Rice and Human Health Risks. *Plants*, 10, 1070.

Zeldowitsch, J. (1934). Über den mechanismus der katalytischen oxydation von CO an MnO_2. *Acta Physicochimica URSS*, 1 (3-4), 449-464.

Zhang, A., Uchiyama, G., & Asakura, T. (2005). pH effect on the uranium adsorption from seawater by a mesoporous fibrous polymeric material containing amidoxime chelating functional group. *Reactive and Functional Polymers*, 63, 143-153.

Zhang, C., Su, J., Zhu, H., Xiong, J., Liu, X., Li, D,m Chen, Y., & Li, Y. (2017). The removal of heavy metal ions from aqueous solutions by amine funtionalized cellulose pretreated with microwave-H_2O_2. *Royal Society of Chemistry,* 7, 34182-34191.

Zhang, J., Li, F., & Sun, Q. (2018). Rapid and selective adsorption of cationic dyes by a unique metal-organic framework with decorated pore surface. *Applied Surface Science*, 440, 1219-1226.

Zhang, W., An, Y., Li, S., Liu, Z., Chen, Z., Ren, Y., Wang, S., Zhang, X. & Wang, X. (2020). Enhanced heavy metal removal from an aqueous environment using an eco-friendly and sustainable adsorbent. *Sci. Rep.*,*10*, 16453.

Zhang, W., Ji, X., Yin, Y., & Wang, C. (2019). Temperature induced color changing cotton fabricated via grafting epoxy modified thermochromic capsules. *Cellulose,* 26: 5745-5756.

Zhang, Y., zhuo, Li, J., Zhao, J., Bian , W., Li, Y., & Wang , X. Jie (2017). Adsorption behavior of modified iron stick yam skin with Polyethyleneimine as potential biosorbent for the removal of anionic dyes in single and ternary systems at low temperature. *Bioresource Technology*, 222, 285-293.

Zhao, Y., Zhan, L., Xue, Z., Yusef, K. K., Hu, H. & Wu, M. (2020). Adsorption of Cu (II) and Cd (II) from wastewater by sodium alginate modified materials. *Journal of Chemistry*, Article ID 5496712.

Zhu, Q., Zhou, R., Liu, J., Jianzhong Sun, J., & Wang, Q., (2021). Recent Progress on the Characterization of Cellulose Nanomaterials by Nanoscale Infrared Spectroscopy. *Nanomaterials*, 11, 1353.

Zuo, Y., He, X., Li, P., Li, W. & Wu, Y. (2019). Preparation and Characterization of Hydrophobically Grafted Starches by In Situ Solid Phase Polymerization. *Polymers*, 11(1), 72.