UNIVERSITI TEKNOLOGI MARA

OPTIMIAIZATION OF SYNTHESIS AND APPLICATION PROCESSES FOR COMPOSITE CROSSLINKED CHITOSAN DERIVATIVES FLY ASH FOR REMOVAL OF REACTIVE RED 120 DYE

IBRAHIM AWAD MOHAMMED

Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Science)

Faculty of Applied Sciences

September 2023

ABSTRACT

Recently, many researchers have been focused on enhancing chitosan by using a physicochemical modification for enhancing the surface structure of chitosan and improving its chemical stability in an acidic environment. In this research work, the adsorption of Reactive Red 120 (RR120) in an aqueous solution onto three biocomposite adsorbents was highlighted. These adsorbents were prepared by loading chitosan with different ratios of Fly Ash (FA) and crosslinking using three different organic crosslinking agents namely: Tripolyphosphate (TPP), Ethylene Glycol Diglycidyl Ether (EDGE), and Epichlorohydrin (ECH). Box–Behnken design (BBD) was applied to optimize five experimental parameters including FA loading ratio (A: 0–50%), adsorbent dose (B: 0.02–0.1 g/100mL), solution pH (C: 4–10), temperature (D: 30 °C–60 °C), and time (E: 20–90 min). Experimental data were analyzed using Langmuir, Freundlich and Temkin isotherm models to evaluate the maximum adsorption capacities of the adsorbents. The composites were characterized using pH point of zero charge (pH_{PZC}), pH-potentiometric titration, elemental analysis, scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, energy-dispersive X-ray (EDX) spectroscopic techniques and BET surface analysis. The BET surface area of the three adsorbents showed significant increase after the loading of FA particles which improve the accessibility of active adsorption sites for the dye molecules and consequently aid the dye adsorption process. The XRD patterns obtained for the studies adsorbents confirmed the successful incorporation of FA particles into the polymeric matrix of chitosan by the identification of characteristic peaks of crystalline planes of quartz (SiO_2), alumina (Al_2O_3), and hematite (Fe_2O_3). The FT-IR spectra prior and after adsorption for each adsorbent confirmed the occupation of the functional groups of the adsorbents by the dye molecules. Furthermore, the surface morphology of the adsorbents after the incorporation of FA particles appeared to be uneven with cracks, pores and spheres (FA particles), whereas after the adsorption process the pores and cracks appear less and the surface is more even. Experimental data obtained were studied to determine the maximum adsorption capacity (calculated from Langmuir equation) for each adsorbent. The maximum adsorption capacity for Chitosan-Tripolyphosphate/FlyAsh, Chitosan-Ethylene Glycol Diglycidyl Ether/FlyAsh and Chitosan- Epichlorohydrin /FlyAsh were found to be 165.8(mg/g), 220(mg/g) and 237.7(mg/g), respectively. Moreover, Adsorption kinetics were compared to Lagergren pseudo-first-order and pseudo-second-order, and results were found to agree better with the pseudo-second-order model for the three studied adsorbents and the adsorption process occurred through chemisorption. Furthermore, the mechanism of the adsorption of RR120 by the synthesized adsorbents was investigated and the electrostatic attraction was identified as the major contributor to the adsorption process. However, hydrogen bonding, Yoshida-H bonding and n-π stacking interactions further assisted in the process of adsorption. The remarkable output of this research can open a window for other possibly significant applications such as treatment of real wastewater, removal of heavy metal ions, and reduction of chemical oxygen demand.

ACKNOWLEDGEMENT

First and foremost, I would like to express my utmost gratitude to my supervisor Dr. Ali H. Jawad Al-Taie for his continuous support of my thesis. Without his patience, motivation, enthusiasm, and immense knowledge I would not be able to complete my thesis. His guidance helped me throughout the entire time of the research and writing of this thesis. I could not have imagined having a better advisor and mentor for my research studies for his efforts have accompanied me from the first day till now. Special thanks to my parents, my sisters and my brothers for their unconditional support, both financially and emotionally throughout my master's degree.

This thesis is heartily dedicated to my mother who has continuously advised and prayed for me throughout the time of my research. She also kept on encouraging me not to give up and strive for what I want in life.

I would to thanks my father he support me through my life until now so my brothers and my sisters through my study.

I would like to thank my cousin AHMED MOUSA for his support and thank my aunt IBRAHIM YOUSEF and my uncles MOUSA, ALI and SAMI.

I would like to thank the staff in UITM specially in the faculty of applied sciences. I would like to thank MR MUMTAZ who helped me greatly during my work in the lab as well as the dean of the faculty of applied sciences. I am indebted to every person involved in my research work and I appreciate those who have contributed to make this research work successful. Only Almighty will bless and reward your kindness. Thank you very much. I would also like to express my heartfelt appreciation to my friends Shahab, Abdulla and Mahmoud for their help and support throughout the course of my studies.

I would to thank my wife for support me. Thanks for Allah . I wish to record my thankfulness to my co-supervisors Dr.Mohd sufri for their continuous inspiration during my research work. I do want to thank the School of Environment and Chemistry and the Graduate School at UiTM Shah Alam for offering me this opportunity to pursue my studies at UiTM. My sincere thanks also goes to the laboratory staff especially Mr. Mumtas Ismail, for their help in all official and technical issues.

Last but not least, I am thankful to the Ministry of Education (MOE), Malaysia for supporting this research project under fundamental research grant scheme (600-IRMI/FRGS/5/3 (340/2019); FRGS/1/2019/STG01/UiTM/02/3).

TABLE OF CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Research Background

Synthetic dyes have been widely employed in different fields of business, including printing, dyeing, textiles, and the leather industries, and this extensive use of synthetic dyes has caused serious harm to the environment (Wan Ngah, et al., 2011). Synthetic dyes, even at extremely low concentrations of about 10 mg/L in water, impart color, rendering them unusable. Additionally, the reactive dyes released into the water are toxic to marine creatures since they cannot degrade. Textile dyes, along with a great number of other industrial pollutants, are extremely toxic, carcinogenic, and possibly mutagenic, which leads to a variety of diseases in both people and animals (Saratale, et al., 2020). Eliminating these colours from the effluents before discharging them into the environment is therefore essential.

The massive cost of conventional techniques for removing pollutants from water and wastewater samples makes it challenging to implement a versatile and economical technique for removing dyes on a large scale. Although some of the current techniques, such as traditional chemical coagulation/flocculation (Ashrafi, et al., 2020), photocatalysis (Chiam, et al., 2020), ozonation (Quaff, et al., 2021) and ion exchange (Ozturk & Silah, 2020) may have acceptable efficiency in eliminating reactive dyes; however, some of them are very tedious to use, expensive and need special equipment. Adsorption is a superior treatment method due to its high efficiency for the elimination of different contaminants such as dyes and heavy metals (HMs), simplicity of design, ease of operation, ability to use a wide range of adsorbents, and the possibility of regeneration of adsorbent (Mok, et al., 2020) (Kumar, et al., 2020). Due to the affordability and effectiveness of adsorption in removing colorants and/or decolorizing textile effluents, it has been identified as one of the most employed wastewater treatment methods in the textile industry. The procedure involves dispersion of wastewater-soluble organic dyes onto the surface of the solid adsorbent.

Chitosan (CS) is a biopolymer obtained from chitin; It has distinctive qualities such as biocompatibility, amino end groups, hydrophobicity, and antibacterial capabilities, and it is the second most prevalent biopolymer (Rajagopal, et al., 2020).