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PREPARATION AND CHARACTERIZATION OF ZINC CROSSLINKED CHITOSAN MEMBRANE AS AN EFFECTIVE ADSORPTION MATERIAL FOR AMOXICILLIN IN PHARMACEUTICAL WASTEWATER

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ABSTRACT
This study aims to synthesize a zinc crosslinked chitosan (Chi/Zn) membrane as an adsorbent for amoxicillin in pharmaceutical wastewater. The Chi/Zn membranes were prepared over 14 hours at 50 °C with varying chitosan and zinc concentrations. FTIR analysis confirmed successful crosslinking by identifying hydroxyl (O-H), carbonyl (C-O), and amine groups (NH_2), along with N-Zn and O-Zn interactions. XRD analysis indicated an amorphous structure, while SEM revealed rough, uneven surfaces. The highest adsorption capacity of a chitosan membrane occurs at a concentration of 60 mg/L. At this concentration, the pure chitosan membrane's adsorption effectiveness and capacity are 42.2% and 42.2 mg/L, respectively. The Chi/Zn membrane adsorbed amoxicillin with an adsorption efficiency of 58.86% with an adsorption capacity of 58.86 mg/g. Thus, it can be said that the chitosan/Zn membrane is quite effective in being applied as an amoxicillin adsorbent in pharmaceutical waste.
Keywords: Chitosan, Zinc, Amoxicillin, Adsorption, Pharmaceutical Wastewater, Membrane
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INTRODUCTION

Wastewater from cities, hospitals, and the drug manufacturing industry brings a diverse range of pollutants, such as pesticides, synthetic dyes, and pharmaceutical residues, into the aquatic environment.[1,2] These substances have the potential to impose detrimental impacts on the ecosystem.[3] Pharmaceutical compounds, especially antibiotics like amoxicillin for the prevention and treatment of bacterial infections, are significant environmental concerns due to their widespread use and low metabolism rates in humans, with 70-90% being excreted unchanged. Studies have found high levels of active pharmaceutical components in surface and groundwater, raising concerns about their toxicity, the development of antibiotic-resistant bacteria (ARB) and genes (ARGs).[4,5] The adverse effect of water contaminants in drinking water has prompted concerns about bad effects to various health issues including cancer, kidney damage and other digestive and health disorders.[6] Their potential to harm microorganisms in wastewater treatment, human cells, and algae communities.[7,8]

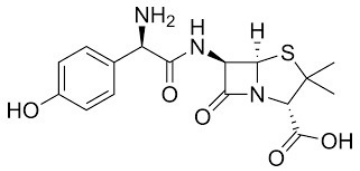


Fig.-1: Amoxicillin Structure

Antibiotic removal from wastewater has been researched using physical, chemical, and biological methods.[7] The majority of these techniques, are expensive (such as membrane technology), require high energy costs

(such as oxidation, coagulation, and electrochemical treatment), high sludge or by-product production (i.e. photochemical and electrochemical treatment), slow process (i.e. biological treatment), and short half-life (i.e. ozonation).[9,10] Adsorption is a widely used technology for removing organic residues from water, attributed to its eco-friendly, cost-effective, and high efficiency. The adsorbate molecules collide with the solid surface, with some adhering to it while others rebound due to chemical and physical interactions.[11,12] Several polymers have been utilized as potential adsorbents for eliminating antibiotics from wastewater. Chitosan stands out among these substances because of its notable features, including hydrophilicity, biocompatibility, low toxicity, biodegradability, exceptional adsorption capacity, and ability to degrade naturally.[13] Chitosan presence of amino and hydroxyl groups, and the ability to eliminate a wide range of pollutants from wastewater. Nevertheless, there are certain obstacles related to its practical application, such as limited selectivity, inadequate mechanical strength, and susceptibility to solubility in acidic environments.[14,15] Chitosan possesses hydroxyl groups and amide groups that enable it to establish connections with polyanion polymers and create polyelectrolyte complexes.[16] Chitosan's adsorption process allows for the selective removal or storage of specific molecules from a solution. Its amino groups (NH_2) can undergo chemical changes to improve its physicochemical and biological properties.[17] Adding a crosslinking agent enhances the membrane's mechanical strength and thermal stability[18]. This modification also improves chitosan's adsorption selectivity and capacity, stabilizes it in acidic solutions, and reduces damage or swelling from gas exposure, thus enhancing its thermal and chemical stability by inducing a negative charge in aqueous solutions.[19,20]

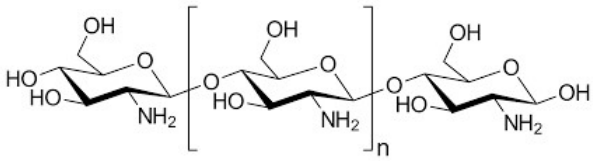


Fig.-2: Chitosan Structure

The zinc solution serves as an ionic bind with the chitosan membrane due to its notable attributes, including potent antimicrobial properties, biocompatibility, high stability, and compatibility with the skin.[21] Zn can be used as a base material for mixing with other compounds due to its favorable ionic size.[22] This study focused on investigating the synthesis, characterization, and adsorption capabilities of novel biocompatible composite Chi/Zn membranes for application as an adsorbent for amoxicillin in pharmaceutical wastewater. Several previous studies indicated that chitosan successfully immobilized zinc oxide nanoparticles. The adsorption tests demonstrated that Chi/Zn is a highly effective and biocompatible composite adsorbent for removing anionic dyes. In other research, MIL101(Fe)/Zn chitosan composite beads are effective for the adsorptive removal and photocatalytic degradation of tetracycline antibiotics.[23] The beads were regenerated with high efficiency in the presence of sunlight. The photo-excitation was due to MIL101(Fe) and Zn, which created the electrons (e^-) and holes (H^+) in the structure. The composite beads are durable and can be repeatedly utilized over an extended duration. The research gap identified in this paper is the lack of studies exploring the use of zinc (Zn) crosslinked chitosan membranes as an adsorbent for amoxicillin in pharmaceutical wastewater. While there have been several studies on using chitosan as an adsorbent to remove antibiotics from wastewater, there is limited research focused on modifying chitosan with crosslinking agents like Zn to enhance adsorption capacity, mechanical stability, and selectivity of the membrane for amoxicillin. This study aims to address this gap by investigating the characterization and performance of Zn-crosslinked chitosan membranes for the adsorption of amoxicillin in pharmaceutical effluents and determining the optimal conditions such as pH, contact time, and adsorbate concentration to improve adsorption efficiency.

EXPERIMENTAL

Material and Methods

The materials used in this study were: the Chitosan standard (CV. Ocean Fresh IPB; Bandung, Indonesia), the amoxicillin standard (Hexpharm Jaya). zinc chloride (Merck; Darmstadt, Germany), acetic acid (Merck; Darmstadt, Germany), and aquadest (UNS Chemistry Sub-Laboratory; Surakarta, Indonesia). The instrument used in this study were: UV-Vis spectrophotometer (Genesys 10s UV-Vis; California, USA), Scanning Electron Microscopy (SEM) (JEOL JSM-6360LA; Tokyo, Japan), Fourier Transform Infrared

(FTIR) spectrophotometer (Shimadzu 8201PC; Kyoto, Japan), X-ray Diffraction (XRD) (Bruker D2 Phaset 2nd Gen; Massachusetts, USA), digital analytical balance (Sartorius, d = 0.001 g; Gŏttingen, Germany), Stirer (Mtops MS300 Hs; Seoul, Korea), oven (Memmert; Schwabach, Germany), orbital shaker (RPR Mixer 0-210RPM, Japan), magnetic stirrer, stopwatch, laboratory glassware (Pyrex; Corning, USA).

Synthesis of Chi/Zn Membrane

The membrane was prepared using chitosan and zinc at weight ratios of 1:1 and 1:2. A total of 1,325 g of chitosan powder was dissolved in 25 mL of acetic acid with a concentration of 2% v/v. The mixture was stirred at a speed of 1000 rpm until a homogenous solution formed. The chitosan solution was left undisturbed overnight to eliminate any dissolved gas. Crosslinking with Zinc, a 5% solution of $ZnCl_2$ was mixed into the chitosan solution, and the resulting blend was subsequently cast into membranes using a PP mold. In the drying process, membranes were dried in an oven at a temperature of 50°C for approximately 14 hours. Membrane preparation for adsorption testing was cut into pieces measuring 2×2 cm, each weighing approximately 0.15 g for subsequent adsorption test with amoxicillin solution.

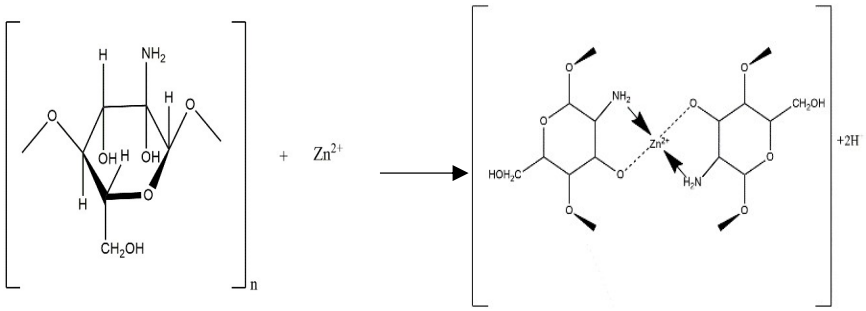


Fig.-3: Chemical Structure Representation of Chitosan Crosslinked by Zinc

Characterization of Chi/Zn Membrane

SEM characterization to determine the surface morphology of the membrane, providing details about its texture, roughness, and structural features. FTIR to determine the functional groups formed in the membrane, confirming the successful formation of chemical bonds and interactions within the material. XRD to determine the crystallinity properties and diffraction pattern of the crystal structure of the membrane, revealing information about its crystal structure and degree of crystallinity.

Analytical Method

A fast and simple without any extraction steps UV-Vis spectrophotometry method was used to determine the concentration of amoxicillin in analytical samples. The calibration curve for quantification was plotted between concentration and absorbance.

Optimization of pH

A 40 mg/L amoxicillin solution was prepared and divided into a series of 100 mL beakers. Each beaker was treated with the chitosan-zinc membrane, and the pH of the solution was systematically adjusted to values ranging from 2 to 8. The solutions were stirred at a constant speed of 120 rpm for 15 minutes to ensure proper mixing and interaction between the amoxicillin and the membrane. After the designated stirring time, samples were taken from each beaker and analyzed using a UV-Vis spectrophotometer to measure the concentration of amoxicillin remaining in the solution, thus determining the optimal pH for maximum adsorption efficiency.

Optimization of Contact Time

A 40 mg/L amoxicillin solution was prepared and poured into a series of 100 mL beakers. A piece of chitosan-zinc membrane was then placed into each beaker, and the solutions were stirred at a constant speed of 120 rpm. The contact time between the membrane and the solution was varied systematically, with samples taken at intervals of 15, 30, 45, 60, 90, and 120 minutes. At each interval, an aliquot of the solution was removed and analyzed using a UV-Vis spectrophotometer to measure the remaining concentration of amoxicillin, determining the optimal contact time for maximum adsorption.

Optimization of the Adsorbate Concentration

A series of amoxicillin solutions with varying concentrations of 10, 20, 30, 40, 50, and 60 mg/L were prepared in 100 mL volumes. Each solution was then contacted with chitosan-zinc (Chi/Zn) membranes under the previously determined optimal pH conditions. The mixtures were stirred at a constant speed of 120 rpm using a shaker for the optimal contact time. After stirring, the concentration of amoxicillin remaining in each solution was measured using a UV-Vis spectrophotometer to assess the adsorption capacity of the membranes at different amoxicillin concentrations.

RESULTS AND DISCUSSION

Synthesis of Chitosan-Zinc (Chi/Zn) Membrane

Figure 4 (a) displays the production of a chitosan membrane, which is brown in color and possesses high tear resistance, this membrane is produced using a basic chitosan membrane-making method without additional crosslinking agents. Figure 4 (b) depicts the Chi/Zn membrane with a 1:1 mole ratio seems to be lighter in color and exhibits improved tear resistance, this suggests that this mole ratio affects the optical and mechanical properties of the membrane, likely due to the interaction between chitosan and zinc at this ratio. Figure 4 (c) demonstrates that the Chi/Zn membrane with a 1:2 mole ratio appears lighter in color and has increased durability, as it is less prone to tearing. This higher mole ratio seems to contribute to the enhanced durability of the membrane, indicating that a higher ratio may result in a more stable structure.

(a) (b) (c)

Fig.-4: Membrane Synthesis Results (a) Chitosan, (b) Chi-Zn (1:1 mol), (c) Chi/Zn (1:2 mol)

The introduction of crosslinking agents in this study led to an enhancement in the brightness of the membrane's color. Additionally, the inclusion of crosslinking agents resulted in a decrease in the flexibility, brittleness, and stiffness of the chitosan membrane. This is significant because these changes in mechanical properties affect the potential applications of the membrane, such as in medical or industrial uses where high mechanical stability is required. The improved tear resistance and color changes indicate that crosslinking could be an effective method to enhance the performance of chitosan membranes in various applications.

Fourier Transform Infrared (FTIR) Characterization

These observations are significant for understanding the chemical environment and interactions within the Chi-Zn membranes, which impact their mechanical and functional properties. The FT-IR spectrum of pure Chitosan (Fig.-5 (a)) exhibited differences from that of Chi-Zn (Fig.-5(b) and (c)). The band of pure chitosan (Fig.-5 (a)) found the band on 3425 cm^{-1} and moved noticeably to wave number 3486 cm^{-1} (Fig.-5 (b)) and 3626 cm^{-1} (Fig.-5 (c)), corresponding to the stretching vibration of hydroxyl (O-H).[14] The effect of crosslinking agent for hydroxyl stretching is the shift in the hydroxyl stretching band suggests interaction with zinc crosslinking agents, which alters the hydrogen bonding environment of the chitosan. The vibrational mode of amide C=O stretching was observed at 1650 cm^{-1} (Fig.-5 (b)) and 1702 cm^{-1} (Fig.-5 (c)) showing the effect of adding crosslinking agent from zinc which shows an increase in peak intensity compared to the pure chitosan curve (Fig.-5) which band at 1710 cm^{-1}. [24] This increase in peak intensity indicates that zinc crosslinking agents enhance the C=O stretching vibration, reflecting an interaction with the amide groups. There is a band of the aromatic ring functional group (C=C) at 1579 cm^{-1}. [25] (Fig.-4(a)) and in the chitosan crosslinked by zinc is also found at 1547 cm^{-1} (Fig.-5(b)) and 1499 cm^{-1} (Fig.-5(c)) with a decrease in band intensity this indicates the vibration of aromatic rings caused by the administration of

zinc as a crosslinking agent. This reduction suggests that the zinc crosslinking affects the aromatic ring vibrations. The decrease in the intensity of the minor band of 898 cm^{-1} (Fig.-5 (b)) and 599 cm^{-1} (Fig.-5 (c)) indicates the presence of vibrations between amide and zinc in N-Zn and O-Zn shows stretching of amide groups interacting with zinc.[21,26]

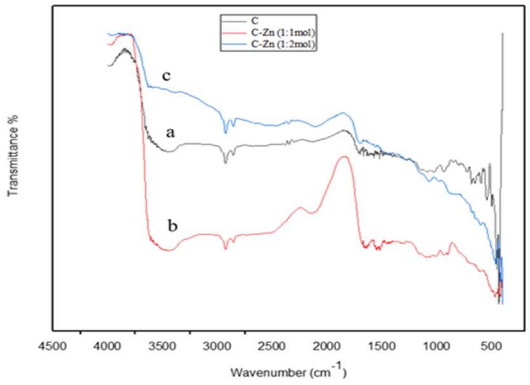


Fig.-5: FTIR Spectra of Pure Chitosan (a), Chi-Zn (1:1 mol) (b), Chi-Zn (1:2 mol) (c)

X-Ray Diffraction (XRD) Characterization

The synthesis of a pure chitosan membrane results in a distinct peak at 2θ 10°–20°, characterized by a strong and acute intensity of diffraction. This peak indicates the presence of a semi-crystalline structure, with a crystalline percentage of 33%. This result reflects the inherent crystalline nature of pure chitosan. In addition, the Chi/Zn A membrane (with a 1:1 mol ratio) exhibits a diffraction band at 2θ 7°–26°, which indicates the presence of a crystalline structure. The strength of this diffraction band is not particularly great, but it clearly shows a peak. The membrane has a crystalline percentage of 27% indicating a decrease in crystallinity compared to pure chitosan. In the Chi/Zn B membrane (1:2 mol), a diffraction peak is observed at 2θ 11°–28° with a low intensity, indicating the presence of a crystalline structure. The crystalline proportion is determined to be 15%, which is lower than both pure chitosan and the 1:1 mol ratio membrane. The decreased crystallinity of the membrane can be attributed to the polymer chain's regularity resulting from the electrostatic interaction and intermolecular hydrogen bond between chitosan and zinc.[21] The shape of the polymer chain is altered through the bonding contact between zinc and chitosan.[27] The regularity of the polymer chain is affected by the electrostatic interactions and intermolecular hydrogen bonding between chitosan and zinc. These interactions disrupt the regular arrangement of the chitosan chains, leading to reduced crystallinity. The bonding contact between zinc and chitosan alters the shape and structure of the polymer chains. This modification in the polymer chain structure results in decreased crystallinity, as evidenced by the lower intensity and shifting of diffraction peaks.

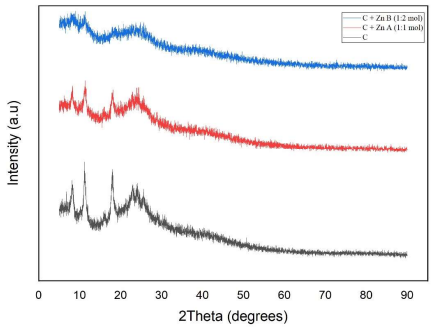
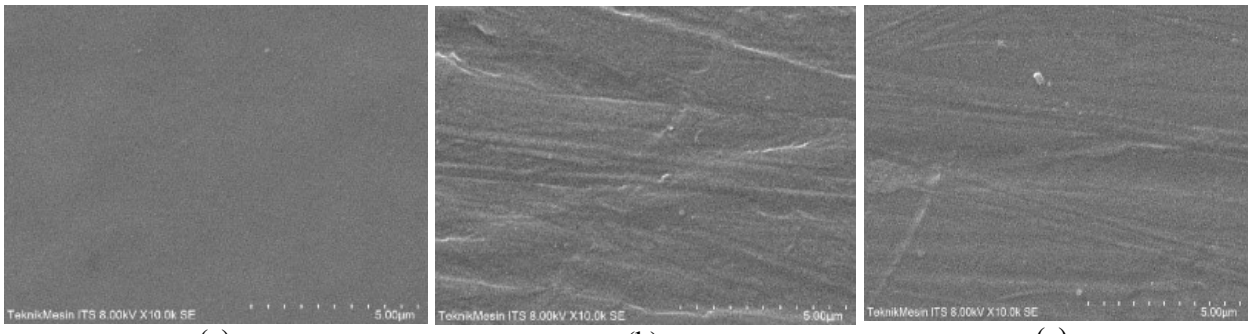


Fig.-6: XRD Spectra of (a) Pure Chitosan, (b) Chi-Zn (1:1 mol), (c) Chi-Zn (1:2 mol)

Scanning Electron Microscopy (SEM) Characterization

Figure-7 (a) shows a pure chitosan membrane that has a flat, fused surface, indicating its stability. The SEM results of Chi/Zn membranes indicate that the surface morphology of these membranes, which contain wrinkles and pores, is rougher and less uniform compared to pure chitosan membranes. This demonstrates

that Chi/Zn has several molecular interactions that can influence the surface morphology of this type. SEM observations indicate that uneven surfaces enhance the adsorption of microparticles. The introduction of crosslinking chemicals leads to a coarser membrane morphology, indicating that these compounds have an impact on the structure of the chitosan membrane and increased roughness of the membrane surface enhances the adsorption of microparticles.



(a) (b) (c)

Fig.-7: SEM Image at the Magnification of 10000× (a) Chitosan, (b) Chi-Zn (1:1 mol), (c) Chi-Zn (1:2 mol)

This results in an increase in both the hydrophobic characteristics and roughness of the membrane surface.[27] The rougher and more hydrophobic surface of the Chi-Zn membranes may affect their performance in various applications. This morphological change can influence the membrane's functional properties, such as its interaction with microparticles and its overall performance in specific applications.

Determination of Optimum pH

The optimal pH of the reagent is the pH of a solution that provides maximum uptake. The results indicate that the optimal pH level for maximum adsorption was 6, which was selected for subsequent steps. Adsorption increased throughout the pH range of 2 to 6 but decreased from pH 7 onwards. This indicates that conditions from pH 2 to 6 are conducive to enhancing the interaction between the Chi/Zn membrane and amoxicillin. Beyond pH 7, adsorption decreased, and the alkaline circumstances promoted the deprotonation of OH^- ions in the Chi/Zn membrane, resulting in repulsive forces between the membrane and amoxicillin. As a result, only a limited quantity of amoxicillin is absorbed. The decrease in adsorption at higher pH levels underscores the importance of maintaining the pH at an optimal level to achieve efficient drug uptake. This finding contributes to optimizing the conditions for practical applications involving Chi/Zn membranes.

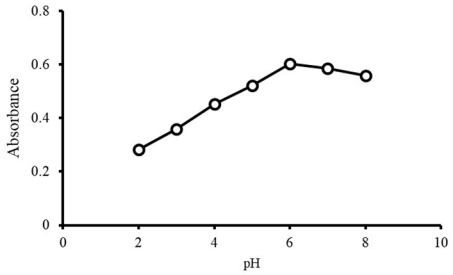


Fig.-8: Amoxicillin Adsorptions on the Effect of Ph

Determination of Optimum Contact Time

Based on Fig.-9, the absorption of amoxicillin solution increases steadily as the contact time increases, until it reaches the optimal contact time. Figure-9 (a) shows that the maximum amount of amoxicillin adsorption in chitosan membranes, without any contaminants, is achieved after 45 minutes of contact time. The adsorption capacity is quantified as 21.53 mg/L, with an efficiency of 32.3%. According to Fig.-9 (b), the Chi/Zn membranes reached their maximum level of amoxicillin adsorption after 60 minutes of contact time. The overall adsorption capacity was measured to be 27.53 milligrams per liter, with an adsorption efficiency

of 41.3%. According to Figure 9 (c), the Chi/Zn membranes exhibit the greatest amoxicillin adsorption when the contact period is 60 minutes. The overall adsorption capacity at this time is 37.53 mg/L, with an adsorption efficiency of 56.3%.

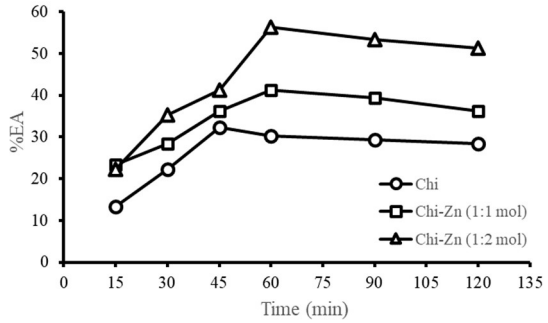


Fig.-9: Amoxicillin Adsorptions on the Effect of Contact Time: (a) Chitosan, (b) Chi-Zn (1:1 mol), (c) Chi-Zn (1:2 mol)

The surface of the chitosan membrane maintains a high level of activity in the adsorption of molecules until 60 minutes. After this point, the adsorption of amoxicillin gradually decreases due to saturation of the adsorbent's surface. This phenomenon arises due to the attainment of equilibrium in the diffusion and attachment of amoxicillin molecules. To avoid the adsorption of amoxicillin by the chitosan membrane, it is necessary to modify the surface. This adjustment is crucial for applications requiring high and sustained adsorption performance.

Determination of Adsorbate Concentration

Figures-10 (a) to 10 (c) demonstrate that as the concentration of amoxicillin increases, the amount of absorbed amoxicillin also increases. In Fig.-10 (a), the graph of pure chitosan membranes demonstrated the highest amount of adsorbed amoxicillin, specifically 42.2 mg/L at a concentration of 60 mg/L, resulting in an adsorption efficiency of 42.2%. Figure-10 (b) displays the Chi-Zn A membrane with the highest amount of adsorbed amoxicillin, measuring 52.86 mg/L at a concentration of 60 mg/L. This corresponds to an adsorption efficacy of 52.86%. Figure-10 (c) displays the Chi/Zn B membrane with the highest amoxicillin adsorption, measuring 60 mg/L at a concentration of 58.86 mg/L, resulting in an adsorption efficiency of 58.6%. This indicates that the Chi-Zn B membrane is more effective in adsorbing amoxicillin. The adsorption process is influenced by the concentration of adsorbate in the solution. Specifically, a higher concentration of adsorbate leads to a greater adsorption power of the adsorbent. Understanding the relationship between adsorbate concentration and adsorption capacity is crucial for optimizing the performance of adsorption systems. The Chi-Zn B membrane's higher efficiency at a slightly lower concentration than its maximum capacity suggests the potential for fine-tuning operational parameters to enhance performance.

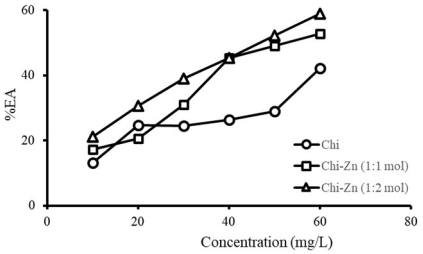


Fig.-10: Amoxicillin Adsorptions on the Effect of Adsorbate Concentrations: (a) Chitosan, (b) Chi-Zn (1:1 mol) (c) Chi-Zn (1:2 mol)

Adsorption Thermodynamic

The adsorption capacity of amoxicillin can be calculated based on the Freundlich isothermal equation and the Langmuir isothermal. The isothermal model corresponding to adsorption is determined by comparing the linearity values of the two equations. The adherence to the Langmuir isothermal model provides insights into the adsorption mechanism and capacity of the membranes.[28] It also helps in understanding the

efficiency of the membranes in adsorbing amoxicillin, which is critical for optimizing their performance in practical applications. Based on the study, it was obtained that the three membranes followed the Langmuir isothermal equation.

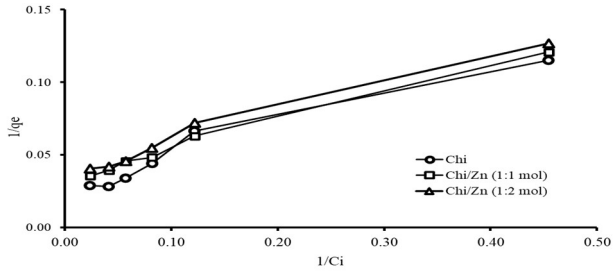


Fig.-11: Chemical Thermodynamics of Langmuir Equations: (a) Chitosan, (b) Chi/Zn (1:1 mol),(c) Chi-Zn (1:2 mol)

Figure-11 (a) demonstrates that the adsorption of amoxicillin by chitosan membranes adheres to the Langmuir isothermal equation, as indicated by the known correlation coefficient values for Langmuir isothermal (R^2 = 0.9458). Figure-11 (b) of the Chi/Zn membrane demonstrates that the amoxicillin adsorption by the chitosan membrane aligns with the Langmuir isothermal equation. The Langmuir isothermal equation is characterized by a known relation coefficient value of R^2 = 0.9874. Figure-11 (c) of the Chi/Zn membrane demonstrates that the amoxicillin adsorption by the membrane aligns with the Langmuir isothermal equation model. The Langmuir isothermal equation has known relation coefficient values, with an R^2 value of 0.995. The Chi-Zn (1:2 mol) membrane shows the best fit with the Langmuir model, as evidenced by its highest R^2 value of 0.995. This suggests that the Chi-Zn (1:2 mol) membrane has the most uniform adsorption sites among the tested membranes. The high R^2 values for all three membranes indicate that the adsorption of amoxicillin onto chitosan and Chi-Zn membranes aligns well with the Langmuir isothermal model. This suggests that adsorption occurs on a homogenous surface with a finite number of identical sites, leading to monolayer coverage of amoxicillin.

Thermodynamic Studies (ΔG)

The value (ΔG) on the pure chitosan membrane is -22,2929 kJ/mol, the value (ΔG) on the Chi/Zn A membrane is -22.292 kJ/mol, the value (ΔG) in the Chi/Zn B membrane -22.6959 kJ/mol. Based on this value, it can be concluded that this indicates that chemical adsorption occurs in the amoxicillin adsorption onto chitosan membranes with the addition of a zinc crosslinking agent.

Adsorption Kinetics

The adsorption rate can be determined by the adsorption rate constant (k) and the contact order derived from a model of adsorption kinetics. The pseudo-second-order model's good fit (high R^2 values) for all membranes suggests that the adsorption of amoxicillin is controlled by chemisorption, where the rate is proportional to the square of the number of adsorbate molecules. This implies that the adsorption process is likely to be limited by the availability of active sites on the membrane. The study found that the membranes exhibited pseudo-second-order as they had a higher linearity.

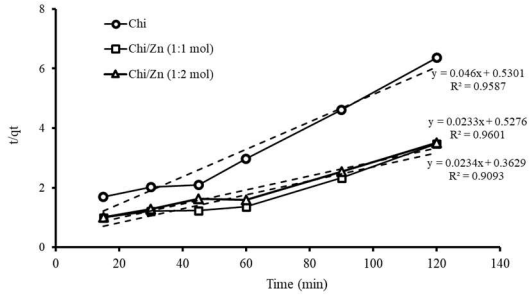


Fig.-12: Pseudo Second-Order Adsorption Kinetics (a) Chitosan, (b) Chi-Zn (1:1 mol), (c) Chi-Zn (1:2 mol)

The study found that the adsorption of amoxicillin by chitosan membranes is best described by the pseudo-second-order kinetic model. The linearity value for pure chitosan membranes, as indicated by the R^2 value for the second-order equation, is 0.939. The R^2 value for the second-order equation in Chi/Zn membrane A

is 0.9503. The R^2 value for the second-order equation in Chi/Zn membrane B is 0.9093. The addition of zinc as a crosslinking agent improves the fit of the adsorption kinetics model. The Chi-Zn A membranes show the highest R^2 value, indicating an enhanced adsorption process compared to pure chitosan. The Chi-Zn B membranes also demonstrate effective adsorption kinetics, though with a slightly lower R^2 value. Understanding the adsorption kinetics is crucial for optimizing the performance of membranes in practical applications. The pseudo-second-order model helps in predicting the rate and efficiency of adsorption, which can guide the design and application of these membranes for effective removal or recovery of amoxicillin.

CONCLUSION

The synthesis of Chi/Zn membranes was accomplished by utilizing the characterization data collected from FTIR, XRD, and SEM. FTIR analysis showed the existence of a hydroxyl group (O-H), a carbonyl group (C-O), an amine group ($-NH_2$), and an interaction between N-Zn and O-Zn. The X-ray diffraction (XRD) examination demonstrates that the chitosan membrane, in the absence of cross-linking agents, displays a crystalline structure. Conversely, the chitosan membrane that is crosslinked with zinc in a 1:1 molar ratio displays a semi-crystalline structure, but the Chi/Zn membrane with a 1:2 molar ratio shows an unstructured or non-crystalline arrangement. The scanning electron microscopy (SEM) analysis shows that chitosan membranes without cross-linking agents have a consistent and even surface structure. In contrast, chitosan membranes that have been cross-linked with Zn have an uneven shape that is characterized by waviness and porosity. From the adsorption study data, the optimal contact time for the Chi/Zn membrane is 60 minutes, the optimal pH of 6, and the optimal adsorbate concentration is 60 mg/L. The chitosan membrane has an adsorption efficiency of 42.2%. In comparison, Chi/Zn membrane A demonstrates an adsorption efficiency of 52.86 mg/L, whi le Chi/Zn membrane B exhibits an adsorption efficiency of 58.6%.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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