

Environmental Friendly Natural Polymer and Its Polylactic Acid Modified Composite Synthesized from *Thais Coronata* Shell for Urea Uptake from Waste Water by Equilibration

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Abstract: CHITOSAN was extracted from *Thais Coronata* shell and modified with poly-lactic acid by gelation method to derive its poly-lactic chitosan nano-composite. Both the chitosan and the polylactic acid modified composite were analyzed using FT-IR and SEM for changes in functional group and surface morphology. A spectrum of unmodified chitosan with absorption bands ranging from 3533 cm^{-1} to 3942 cm^{-1} , all attributed to O-H stretching vibrations, and a cluster of bands attributed to N-H stretching vibrations of primary and secondary amine at 3417 cm^{-1} , 3317 cm^{-1} , 3286 cm^{-1} , and 3217 cm^{-1} . The $-\text{NH}_2$ stretching is approximated matched by the high and deep adsorption peak at 1496 cm^{-1} corresponding to Amide II, which is a characteristic band of N-acetylation. SEM images of unmodified and poly-lactic acid modified chitosan composites at 500 and 1500x magnification reveals a rough surface with significant pores, typified and notable irregularities that are ideal for adsorption. The morphology of the poly-lactic acid modified chitosan has changed significantly in relation to its weak surface properties, with a smoother surface domain and reduced pore structure. The degree of ionic activity between chitosan and the poly lactic acid grafted onto the polymer chain is linked to morphological variability. The samples were investigated as potential bio-sorbents for urea uptake from waste water by equilibration. Adsorption experiments were conducted on 20100mg/L urea wastewater and the effect of contact time, concentration, temperature and pH on urea removal efficiency was studied. At temperature of 30°C and pH of 2.5, maximum removal efficiency of 50.16 and 54.33% were obtained for the modified and un-modified chitosan respectively. Results from adsorption studies revealed that the modification with poly-lactic acid did not enhance adsorption capacity of chitosan, although its solubility and resistance to acidic degradation was improved. The development of chitosan materials with better adsorption capacity in the light of urea uptake is therefore very feasible.

Keywords: Nanocomposite, Polylactic Acid, *Thais coronata* Shell, FT-IR and SEM

1. Introduction

Urea (carbamide) is a central molecule in the narration of modern chemistry because it allows synthetic organic chemistry to be explored. It is one of the most widely synthesized organic compounds currently available [27]. Due to its extensive use, it is usually produced in large quantities. Urea is highly rich in nitrogen and as such the primary constituent of most nitrogenous based product. Over 90% of the world's urea industrial output is directed toward nitrogen-based fertilizers [15]. The reaction of carbon dioxide with ammonia at high pressure is used in the industrial synthesis

of urea. The Snamprogetti process (which involves NH_3 stripping), the Stamicarbon process (which involves CO_2 stripping), the IDR process and the ACES process are the modern urea processing technologies [4].

The waste produced during urea processing, on the other hand, is a problem that must be addressed. The urea synthesis evaporation process produces the most significant amounts of urea wastewater. Urea enters the environment from a variety of routes, including leaching from agro-breeding farms and fields, byproduct of mammalian protein metabolism and mostly effluents from production plants. The elimination of urea from wastewater is required, because urea wastewater poses a

serious threat to both man and his environment, especially the aquatic environment. These threats are made manifest by problems arising from eutrophication (algal bloom, increase of toxins, depletion of dissolved oxygen, and death of marine lives), nitrate accumulation (which subsequently lead to nitrate poisoning with direct impact on man), ammonia volatilization, phyto-toxicity, heavy metal deposition and other instabilities which alter the desired state of the aquatic ecosystem. Even though urea is biodegradable, its emission potential is increased due to its slow degradation rate [3].

Chitosan, as a biosorbent, has a number of distinct advantages over other synthetic sorbents. The low toxicity, highest biodegradability, natural availability and low production cost are among them. However, low surface area and porosity, the poor mechanical and thermal stability, limited solubility in aqueous solutions, resistance to mass transfer, high molecular weight, formation of very viscous and flow resistant hydrogels even at low concentrations and sensitivity to environmental pH changes (soluble in specific acidic medium) are all drawbacks of this low-cost biosorbent [7]. These shortcomings limit the practical applications of chitosan [29].

Chitosan is well known for having typical polysaccharide properties as biodegradability, non-toxicity and biocompatibility while also having exclusive properties such as chelating ability, film-forming ability, antimicrobial properties and adsorption properties. This natural biopolymer with such interesting properties has sparked a lot of interest in a variety of potential new applications, and it's now broadly generated commercially, mainly from seafood waste. The shells of snails make up a significant bit of the raw seafood products thrown away as waste. Since these shells are insoluble and non-biodegradable, they take up a large amount of space in the environment, thereby polluting it. As a result, a waste-to-wealth strategy for chemically transforming these shells into a value-added material like chitin and chitosan is needed. Several methods for extracting chitin and deacetylating it to make chitosan are being researched and developed, and have sparked a lot of interest recently [8].

Chitosan and its derivatives currently have over 200 applications, and this number is growing [1]. Chitin is primarily used as a starting material in the production of chitin-derived products like oligosaccharides, glucosamine and chitosan [5]. Chitosan with its exclusive properties: biodegradability, biocompatibility, non-toxicity, adsorptive properties and solubility in specific acidic medium, gives it a wider sphere of industrial usage. The analysis of chitosan as a significant environmental treatment material to remove metal ions, as well as other inorganic and organic pollutants from wastewater is one of the noteworthy developments in the current range of applications [6, 10]. Tissue engineering, Cell culture, dietary supplements, drug delivery, food processing, water treatment, cosmetics, agriculture, paper and pulp, and other medical applications are also areas where chitosan has displayed great promise [1, 14, 16].

A lot of work has been reported in developing physicochemical modification processes to comprise several forms of functionalization in the polymer. Chemical

modifications such as alkylation, oligomerization, quaternization, acylation, carboxyl alkylation, hydroxyl alkylation, sulfation, thiolation, enzymatic modifications, graft copolymerization and phosphorylation have been performed, allowing for the modification of properties for end uses in a wide range of fields [18]. Researchers have created a range of chitosan products using chemical and physical methods, including membranes, gel beads, fibers, film, powders, porous frameworks, hollow fibers, nanocomposites, and sponges [12]. It has been discovered that certain chemical modifications can improve its chemical stability and flexibility, improve its adsorptive properties, and reduce its sensitivity to acidic media. Among the numerous deployed modification processes that have contributed immensely to the novel application of chitosan molecule is the co-polymerization with polylactic acid which has resulted to a copolymer with renowned properties and diverse application. Polylactic acid chitosan has become important in biomedical and medical applications, such as tissue engineering and drug delivery systems, owing to its higher resistance to acidic degradation, improved sorption capability, non-toxicity, improved thermal stability, and preservation of biocompatibility and biodegradability [26]. It also has a wide array of environmental based applications. But, in the environmental sphere, its latent has been underutilized [26]. However, in recent years, many processing processes and final applications of chitosan polylactic acid nanocomposite have posed an appealing subject of current nanoparticle research.

Although different configurations of chitosan modification including cross linking with both natural and synthetic polymers have been published [25, 30].

There are many urea removal methods, but the majority of them are either in development or are very expensive. In terms of physicochemical efficiency and scientific process, the techniques vary. Enzymatic hydrolysis, hydrolysis, catalytic decomposition, adsorption, electrochemical oxidation and decomposition in the biological bed and by strong oxidants are some of the most common treatment ways [27]. Among the numerous urea effluent treatment methods, adsorption onto low cost bio-sorbents has pointed out simple, effective, economical, and environmentally friendly. Adsorption-based removal technologies using adsorbent materials such as chitosan and poly lactic acid can thus be used for the elimination of nitrogen-containing species such as urea and nitrate [23-24]. Although, the molecular level details for urea up-take by chitosan and chitosan-based sorbents have been poorly reported [13]. This paper reported the removal of urea from urea wastewater using chitosan and its Poly-lactic acid nanocomposite synthesized from shell of *Thais Coronata*.

2. Materials and Methods

2.1. Sample Collection and Preparation

The discarded *Thais Coronata* shells were sourced from Borokiri market, a prominent market in Port Harcourt

Municipality, Rivers state. The shells were sorted and thoroughly washed to remove any soluble organic materials, adherent proteins, or other contaminants. They were then dried in the oven at 80°C for 24 hours before grinding with a mechanical grinder.

2.2. Extraction of Chitosan

With minor modifications, the chitosan was extracted using a method proposed by (Wan et al.,) [29]. The ground shells were deproteinized for 1 hour at 70°C in a 1M NaOH solution with continuous stirring and a solid-to-solvent ratio of 1:10 (w/v). The boiled sample was removed, put in a hood, and left to cool for 30 minutes at room temperature. The shells were then filtered, vigorously washed with distilled water until they reached a neutral pH, and oven dried to eliminate all moisture. The next step in the process was to demineralize the sample with 1 M HCL at 70°C for 1 hour while maintaining a 1:10 (w/v) ratio. The sample was also purified before being washed with distilled water and dried in the oven. The chitin was then deacetylated by boiling it in 12.5M NaOH (50 percent) for 2 hours at 90°C. It was then repeatedly washed and filtered (to achieve a neutral pH), oven-dried, and allowed to cool to room temperature.

2.3. Synthesis of Poly Lactic Acid-Chitosan Nanocomposite

Ionic gelation was the method deployed in producing poly-lactic acid chitosan nanocomposite.. Firstly, a 2 percent chitosan solution was prepared by dissolving 2g of of chitosan in 100ml of 1% acetic acid. This yielded a positively charged gel-like solution with pH of 3.5. The production process proceeded by mixing the chitosan solution with 3% polylactic acid in trichloromethane. After vigorous stirring and ultrasonifying the mixture for 25 minutes, 2% sodium tripolyphosphate was introduced. Sodium tripolyphosphate is a reticulating agent, added to the solution to preserve and improve the crushing strength of the nanocomposite to be formed. Chitosan poly lactic acid nanocomposite was gradually formed upon further intense stirring. Finally, the mixture was centrifuged at 6500rpm for 30 minutes and then lyophilized in a dryer to recover the nanocomposite from solution [20-21, 26].

2.4. Characterization of Synthesized Chitosan Samples

Scanning electron microscopy and Fourier Transform infrared spectroscopy was used to characterize the chitosan samples and justify the effectiveness of their respective preparatory methods.

2.5. Solubility Test

Although a detailed characterization method can precisely help us identify the compound, but a preliminary test gives us a clue about the success of the production sequence. Chitosan exhibit different behaviour in different aqueous media, hence, solubility test provides a great information about the synthesized products since chitosan is known to be insoluble in water and soluble in common organic acid such as acetic acid [1].

Both the chitosan and the poly lactic acid nanocomposite

were subjected to solubility test in four (4) different solvents: Distilled water, Acetic acid (1- 2%), trichloromethane (chloroform) and acetone. 0.5g of both the modified and unmodified sample was dissolve in 50ml of the respective solvents at room temperature. After 3 hours of slight agitation, the solution was filtered, and the percentage soluble content was calculated from the difference in weight between the original sample and the final weight of the residual sample obtained on the filter paper.

2.6. Urea Waste Water Analysis

Urea wastewater was sampled on-stream from a urea production plant, located at Onne. River State. Nigeria. Four (4) drain points from different wastewater distribution line were explored, prior to being subjected to the designed treatment process (desorption/ hydrolysis). The Wastewater sample were labelled D1, D2, D3 and D4, corresponding to the respective drain points investigated. The wastewater samples with temperatures ranging between 65- 75 °C were cooled and their urea concentration was quantified using spectroquant pharo 300 UV- spectrophotometer at wavelength of 436 nm. They were determined to be 20100, 12050, 6250, 1160 mg/l corresponding to D1, D2, D3 and D4 samples respectively.

2.7. Quantitative Analysis of Urea

For the quantification of urea, the chemical derivatization method was deployed using dimethyl amino benzaldehyde (Erlch reagent) as the spectrophotometric reagents [11], and 2M H₂SO₄ as the conditioning acid. DMAB (Erlch reagent) has the benefit of reacting with urea at room temperature to create a chromogen that emits a yellow-green color that can be used in the quantitative and qualitative estimation of urea, unlike the other widely used reagents monoxime and diacetyl thiosemicarbazone, which involve higher temperatures [2].

2.8. Batch Adsorption Study

The urea absorption from the wastewater samples was conducted in batches. Erlenmeyer flasks with ground glass stoppers was used for adsorption experiment. 20ml of known-concentration urea wastewater was transferred to separate 100ml flasks, and 0.2g of the derived chitosan was accurately weighed into the flasks. The flask was put in a water bath shaker and permitted to stand for a certain amount of time at a set temperature (30 minutes). After which, the mixture was filtered using the Whatman NO 2 filter paper. 10ml of the filtrate were then analyzed using same analytical procedure described in the preliminary adsorption experiment above.

The adsorption procedure was carried out with variations in initial urea concentration, contact time, temperature, and pH for both unmodified and modified chitosan (Poly-lactic acid chitosan composite), while the adsorbent dose and stirring rate (rpm) were kept constant. The removal efficiency of unmodified chitosan and lactic acid- nanocomposite (modified chitosan) was measured using the following formula:

$$\% \text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i and C_f denote the initial concentration and final residual concentration of urea in mg/L respectively.

2.9. Initial Concentration

The effect of varying the concentration on the adsorption process was investigated by pouring a 20 ml solution of the various wastewater samples D1, D2, D3, and D4 (with known concentrations of 20100mg/L, 12060mg/L, 6250mg/L, and 1160 mg/L, respectively) into a 100 ml flask along with 0.2g of unmodified chitosan into a water bath shaker set at 25°C for 30 minutes. Same adsorption procedure was conducted using the modified chitosan, and their respective concentrations after adsorption were determined.

2.10. Contact Time

20ml of D1 urea wastewater sample and 0.2g of unmodified chitosan sample were transferred to separate 100ml flasks and put in a water bath shaker held at 25°C for 5, 10, 20, 30, 50, and 60 minutes, respectively. Same adsorption procedure was also adopted using the modified chitosan and their respective concentrations after adsorption were determined.

3. Results and Discussion

3.1. Solubility Test

The solubility of chitosan and Poly- lactic acid modified chitosan composite in different solvents are presented in Table 1.

Table 1. Solubility of chitosan and poly-lactic acid chitosan nanocomposite.

Solvents	% Soluble Content (UMC)	% Soluble Content (MDC)
Water (H ₂ O)	1.22	4.20
1% Acetic Acid	90.40	80.55
2% Acetic Acid	95.82	86.46
Chloroform	0.15	0.19
Acetone	0.21	0.24

The percent solubility of modified and unmodified chitosan differed according to the report. Chitosan was very soluble in acidified aqueous solution. It showed 90.4 and

95.82% solubility as against poly -lactic acid modified chitosan which showed 80.55% and 86.46% in 1 and 2% acetic acid respectively. The changes observed in poly lactic acid chitosan's lower solubility content in acidic medium indicates that acidic degradation has improved, and this improvement can be attributed to the depletion of the amino group present in the copolymer and hence the protonation of -NH₂ in acidic medium, which is responsible for the solubility of chitosan was hampered.

Furthermore, Chitosan with a higher protonated amino group content readily forms well-bordered arrangements in the Van der Waals force and hydrogen bond, outperforming its propensity for intramolecular chemical bonds (Zhang *et al.*, 2012, He, Chen and Dong, 2001). This explains its partial solubility in hydrogen-containing solvents and its solubility in acidic medium. The unmodified chitosan floated on water without agitation and had a higher percentage insolubility (1% soluble content), while the Poly-lactic acid modified chitosan was only sparingly soluble in water (about 4% soluble content). Hydrophilicity was however slightly improved in the poly-lactic acid modified chitosan (MDC). [13], published similar result. In acetone and chloroform, both the unmodified and poly-lactic acid modified chitosan are insoluble. The low percentage solubility in acetone and chloroform (less than 1% soluble content) found in this study may be due to sample loss during filtration and drying.

3.2. SEM Analysis for Chitosan and Modified Chitosan

SEM micrograph may be used to investigate the surface area and morphologies of different adsorbents [22]. SEM images of unmodified and poly-lactic acid modified chitosan composites at 500 and 1500x magnification are shown in Figures 1 and 2, respectively. The unmodified chitosan micrograph (Figure 1) reveals a rough surface with significant pores, typified and notable irregularities that are ideal for adsorption. Figure 2 shows that the morphology of the poly-lactic acid modified chitosan has changed significantly in relation to its weak surface properties, with a smoother surface domain and reduced pore structure. The degree of ionic activity between chitosan and the poly lactic acid grafted onto the polymer chain is linked to morphological variability.

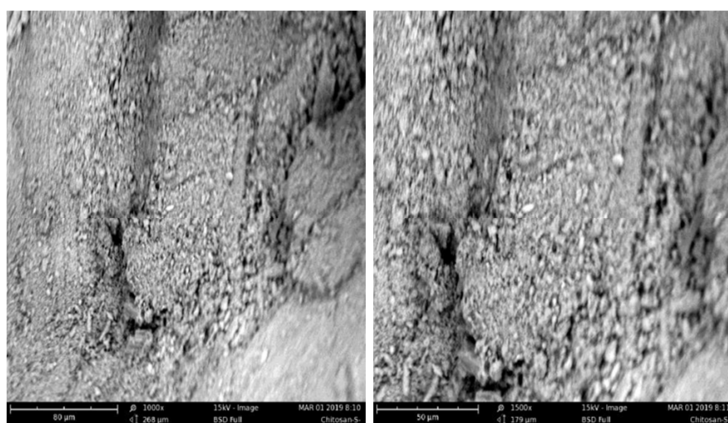


Figure 1. SEM footage for unmodified chitosan at 15kV, 500 and 1500× magnification.

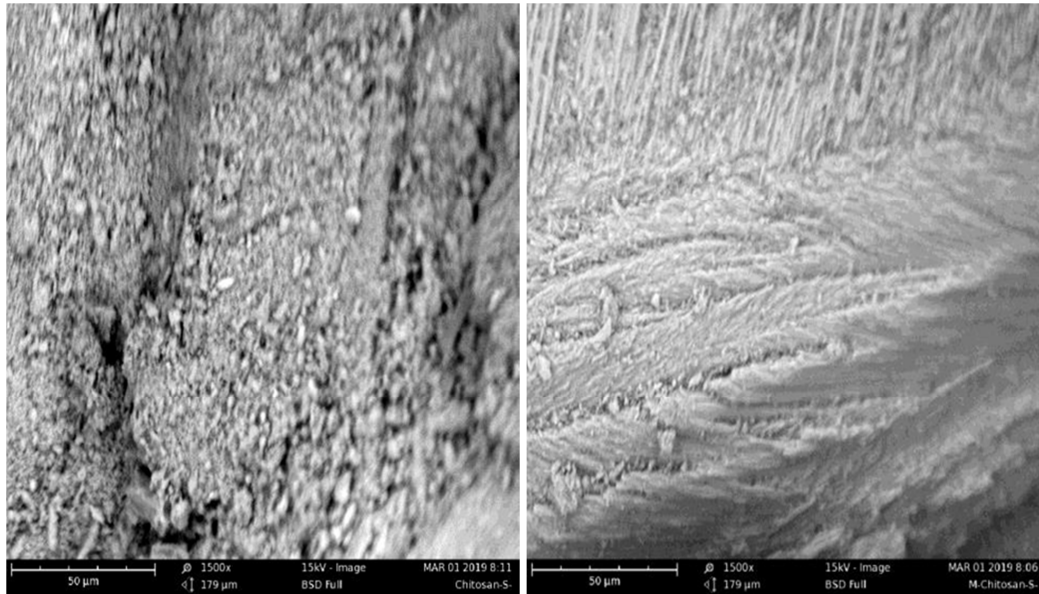


Figure 2. SEM footage for poly-lactic acid modified chitosan at 15kV, 500 and 1500 \times magnification.

3.3. FT-IR Analysis of Chitosan and Modified Chitosan

Chitosan is a biomaterial with several active binding sites. FTIR spectrometer was used to classify the active groups of the derived chitosan composite before and after poly-lactic acid alteration. The spectrum of unmodified chitosan and poly-lactic acid modified chitosan is shown in Figures 3 and 4, respectively.

Figure 3 shows a spectrum of unmodified chitosan with absorption bands ranging from 3533 cm^{-1} to 3942 cm^{-1} , all attributed to O-H stretching vibrations, and a cluster of bands attributed to N-H stretching vibrations of primary and secondary amine at 3417 cm^{-1} , 3317 cm^{-1} , 3286 cm^{-1} , and 3217 cm^{-1} . The $-\text{NH}_2$ stretching is approximated matched by the high and deep adsorption peak at 1496 cm^{-1} corresponding to Amide II, which is a characteristic band of N-acetylation that is derived primarily from in-plane N-H bending and incorporates the futures of amines and ketones (Islam *et al.*, 2011). The stretching vibrations around 748 cm^{-1} , 871 cm^{-1} ,

949 cm^{-1} corresponds to C-H bending of the substituted chitosan groups and the observed peaks at 1681 cm^{-1} and 1805 cm^{-1} can be attributed to C=O and C=O stretching, respectively.

Comparatively, the spectra of modified chitosan (Figure 4) show the different vibration which occurred after modification. The emergence of vibration at 3225 cm^{-1} and 3178 cm^{-1} corresponds to O-H stretching of carboxylic acid which showed that the Poly- lactic acid modification process was successful. Also, the vibration at 1519 cm^{-1} which represents $-\text{NH}_2$ (Amide II) stretch has been substantially reduced, indicating a depletion in the $-\text{NH}_2$ constituent of chitosan after modification. This depletion can also be interpreted by the disappearance of the clustered peaks attributed to N-H vibrations in Figure 4. However, the vibration at 3402 cm^{-1} corresponds to N-H stretching of the residual amines. The other bands observed were at 1041 cm^{-1} , 2345 cm^{-1} , 1705 cm^{-1} and 1836 cm^{-1} corresponding to CO-O-CO, O=C=O and C=O vibrations, respectively.

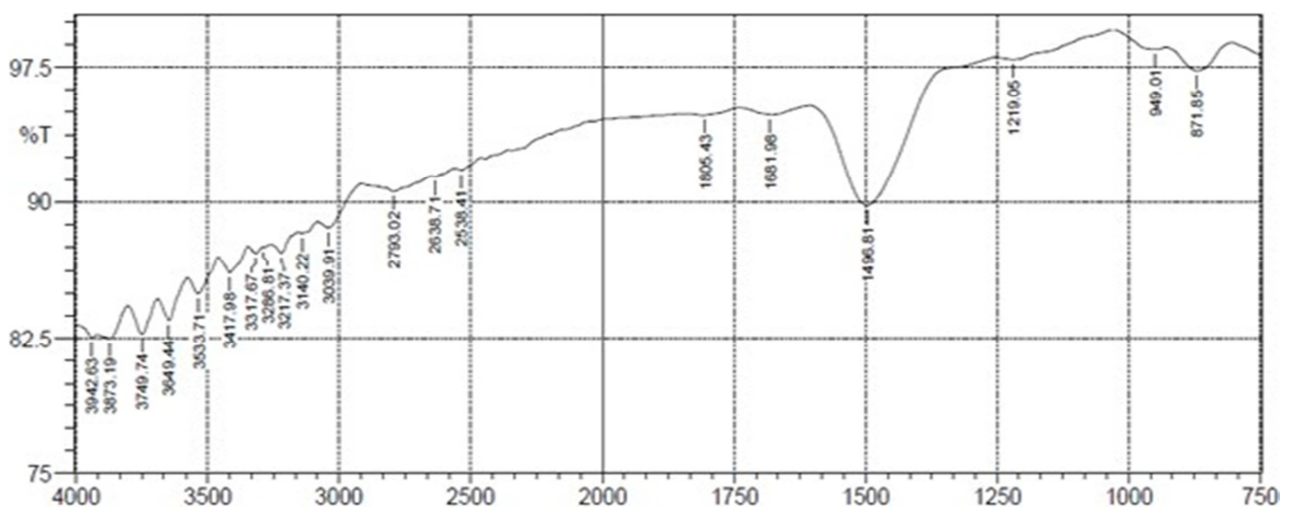


Figure 3. FT-IR Spectrum of unmodified Chitosan.

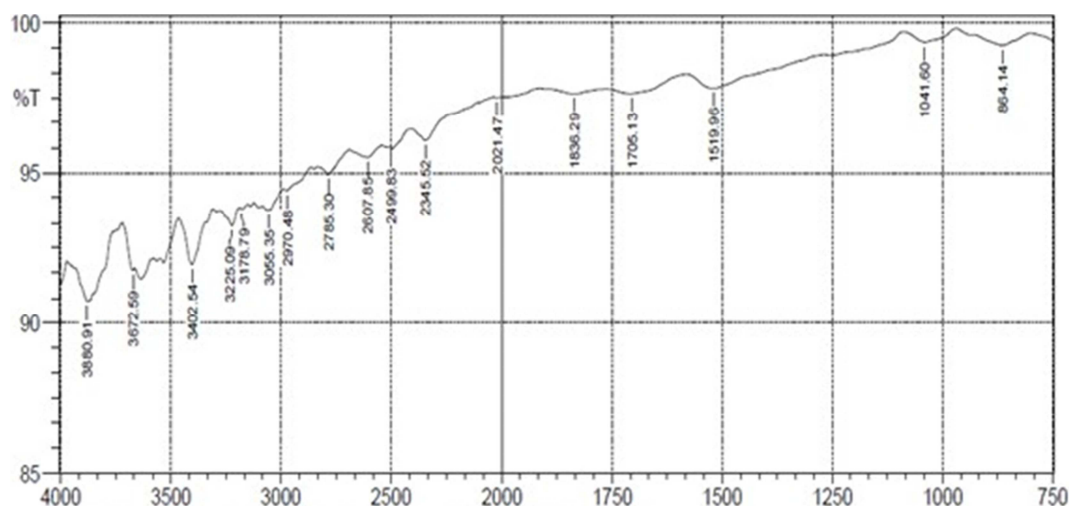


Figure 4. FT-IR Spectrum of poly-lactic acid Modified Chitosan composite.

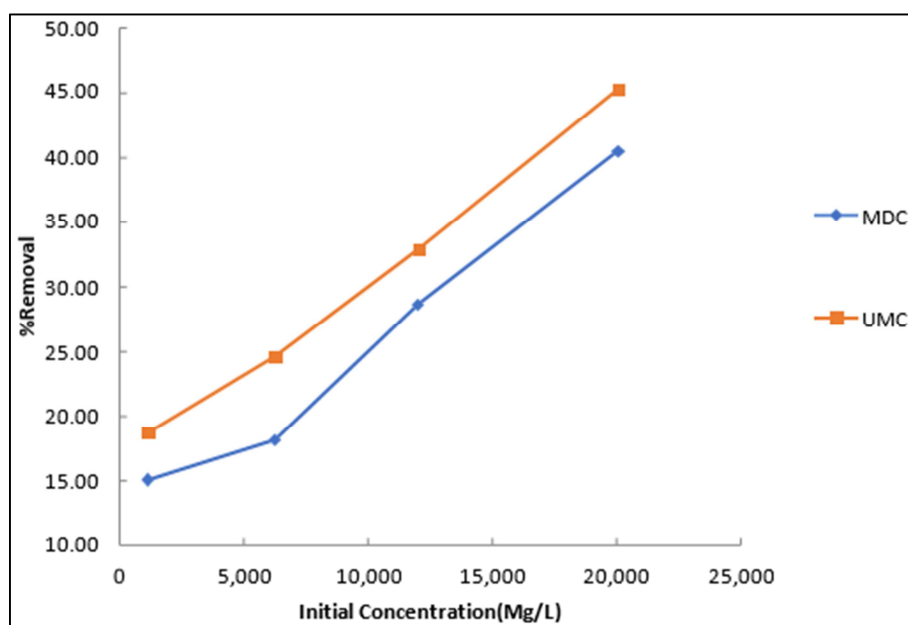


Figure 5. Concentration Profile.

The adsorption experiment was carried out on various wastewater samples, and the findings shown in Figure 5 indicate a growing trend in percentage urea removal as the initial concentration increases, for both unmodified and modified chitosan. The ability of surface functional groups to bind ions in solution and the fact that higher concentrations have sufficient active groups explain this adsorption pattern. In other words, increased concentration acts as a driving force for ions transiting from the aqueous to the solid phases to overcome mass transfer resistance [17]. As a result, the adsorption potential of the adsorbents improved as the concentration of urea in solution increased [19]. The unmodified chitosan adsorbent however showed a stronger adsorptive strength than the modified, with maximum percentage removal of 45.22 and 40.41% respectively for the D1 sample with initial concentration of 20100 Mg/L. This observation agrees with the FT-IR spectrum of the unmodified sample which displays more active sites suitable for

ionic interaction and subsequently, greater adsorption.

3.4. Effect of Contact Time

One of the main factors typically measured in batch adsorption experiments is the determination of the optimum contact time needed to achieve the highest adsorbate removal. However, equilibrium time is one of the most important factors to consider when choosing a wastewater treatment facility [9]. The percentage of urea removed increased as contact time increased before equilibrium was achieved, according to the findings. Other variables such as adsorbent dosage, temperature, and pH of the solution remained unchanged. It's possible that the rise in percentage removal with increased contact time is due to more time being available for the urea-chitosan interaction. Due to the wide surface area available for adsorption, both adsorbents showed a rapid urea absorption in the first 20 minutes of contact, followed by a slower adsorption

rate as the active site was filled.

According to the findings, urea removal increased as contact time increased from 5 to 40 minutes for both adsorbents, although the adsorption rate did not change significantly because they appear to reach equilibrium at 40–60 minutes. For unmodified and modified chitosan, respectively, removal rates of 40.41 percent and 45.22 percent were obtained. The unmodified chitosan's higher adsorption ability can be due to its surface morphology, which has more substantial pore spaces appropriate for

adsorption, as shown in SEM footage (Figure 1). There were no major differences in the percentage of urea extracted after 40 and 50 minutes for both modified and unmodified chitosan, according to the profile. The interval between 40 and 50 minutes reflects the equilibrium time at which the adsorbents are thought to have reached an equilibrium concentration C_e . Figure 6 shows that the adsorption profile follows a linear pattern at first, then a flat plateau-like pattern. This is certainly because of the rapid occupation of the most readily available adsorbing sites on the adsorbent surface.

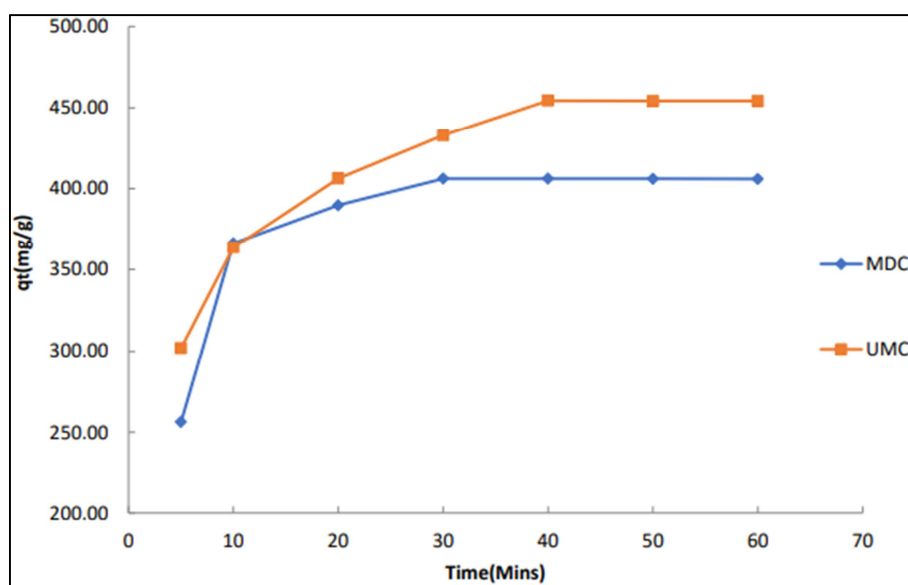


Figure 6. Contact Time Profile.

4. Conclusion

The synthesis of chitosan from non-biodegradable snail shell has proven useful in waste reduction and has also shown great potential in the remediation of urea wastewater by adsorption. Although results confirmed that the modification of chitosan using poly lactic acid resulted to a compatible and promising co-polymer, but its capacity to adsorb urea was not significantly enhanced due to the depletion of amino group on the parent chitosan polymer chain which mostly dictate the chemical reactivity of a large number of chitosan based materials.

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