Chitosan Epoxidized Natural Rubber Biocomposites for Sorption and Biodegradability Studies

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ABSTRACT: The slow-release mechanism of copper into soil followed by soil biodegradation was studied using the chitosan (CTS)/epoxidized natural rubber (ENR) biocomposite. The biocomposite was prepared by homogenizing CTS in ENR50 (ENR with about 50% epoxy content) latex in the presence of curing agents and acetic acid. It was found that the adsorption property of the biocomposite was very much influenced by chitosan loading, where 20phrCTS-t-ENR biocomposite can absorb 76.31% of Cu(II) ions. The desorption study indicates that the copper (II) ion can be released at a very slow and control phase as proven by the kinetic study using zero-order, first-order, Higuchi, and Korsmeyer Peppas equations. The slow-release studies comply with the Higuchi square-root equation, indicating that the release process is diffusion-controlled. Results of desorption and biodegradation process suggest that this biocomposite has the potential use of being a slow-release matrix in the field of agriculture.

INTRODUCTION

Over the years, many ecological and economic problems are related with the extreme use and misuse of fertilizers in the agricultural field. To overcome these problems, the use of slow-release fertilizers has been introduced. This method has been proven to be a promising key to various environmental problems caused by old-fashioned water-soluble fertilizers. With slow-release fertilizers, the required amount of fertilizer is lowered, the efficiency of fertilizer is improved, the active ingredients are protected from early degradation, and environmental pollution problems are practically negligible.

One of the main issues in producing or developing slow-release fertilizers is the utilization of an appropriate biodegradable material in the matrix. Poly(butylene succinate) (PBSU) is widely used due to its potential, but it is a costly material. Therefore, to obtain a low-cost material, PBSU has been blended with starch. Polymer-coated conventional slow-release fertilizers have been widely developed lately.

Chitosan (CTS) being one of the most abundant natural polymers on earth is classified under polysaccharides and known to be biodegradable. Chitosan is a linear polymer of a (1 → 4)-linked 2-amino-2-deoxy-p-D-glucopyranose obtained from N-deacetylation of chitin, which is mainly found in crustacean. In the beginning, chitosan was found to be very useful in wastewater treatment due to its nature to chelate metallic ions and the presence of the amino (−NH₂) and hydroxyl (−OH) groups. This has triggered a lot of researchers to explore the adsorption of various metals from aqueous solutions using chitosan and modified chitosan.

Even though chitosan is a good and competent metal absorbent, its usage is limited due to the powder form of chitosan, which involves a high cost due to the filtration process. Therefore, we attempt to find a better and cheaper solution by introducing a chitosan rubber biocomposite using the entrapment method. Incorporation of CTS in a rubber matrix may further extend its capability on the variable release behavior of fertilizer due to the double advantages of entrapment of the polymer and sorption by CTS.

In this work, we report the development of a slow-releasing copper compound based on the entrapment of CTS in ENR50. The entrapment method allows a matrix to be noncovalently but steadily altered with water-soluble polymers, whereas
copper is known to be a micronutrient in fertilizers and 
required in a small amount as a nutrient for food, and fiber 
production in agriculture. Desorption and biodegradation 
studies were carried out to determine the likelihood of this 
material to be used as a slow-release material in the future.

MATERIALS AND METHOD
Epoxydized natural rubber latex with 50% epoxy content 
(ENR50) was supplied by the Malaysian Rubber Board. The 
actual epoxy content was determined by means of NMR 
spectroscopy using a Bruker Avance-400 NMR spectrometer 
to be 51.05%. Chitosan (CTS) with % degree of deacetylation 
≈ 90 was provided by Advanced Materials Research Center, 
Kulim, Kedah, Malaysia. The weight-average molecular weight 
(Mw) of the chitosan was determined by means of size 
exclusion chromatography to be 105 100 Da. The other 
compounding ingredients used were zinc oxide, stearic acid, N-
cyclohexyl-2-benzothiazole sulfonamide (CBS), zinc oxide, stearic acid, and sulfur, which were all purchased from 
Bayer (M) Ltd and used as received. Cu(II) stock solution 
(1000 ± 2 mg/L) was purchased from Merck.

Processing of CTS-t-ENR Biocomposite with Different 
Chitosan Loading. CTS (5.0 g) was added to 100 mL of 2% v/v acetic acid to form a slurry. Then, known quantities (2.5, 5, 
10, 15, and 20phr) of this slurry were added to ENR50 latex 
and mixed using a high-speed homogenizer at ambient 
temperature (27–30 °C) for 2 min. Subsequently, the 
remaining compounding ingredients were added with 
different mixing for another 3 min. The compounded 
materials were cast on a glass mold and set to air-dry at ambient 
temperature for 24 h before placing in an oven at 60 °C for an 
additional 24 h. The biocomposites obtained are designated 
herein as 2.5phrCTS-t-ENR, 5phrCTS-t-ENR, 10phrCTS-t-ENR, 15phrCTS-t-ENR, and 20phrCTS-t-ENR.

Method for Copper-Ion Adsorption–Desorption 
Study. Cu(NO3)2 stock solution (1000 mg/L) from Merck 
was diluted into 100 mg/L as a standard solution. Then, this 
standard solution was diluted further into 0.5–2.0 mg/L 
concentration for calibration. Cu(II) standard solutions (100 
mg/L) were diluted to 25.0 mg/L and 50.00 mL. The pH of 
these solutions was maintained between 5.5 by adding an 
appropriate amount of either 0.01 M HCl or 0.01 M NaOH.

Adsorption Experiments. Each biocomposite CTS-t-ENR 
(0.20 g, prepared from ENR50 latex and with different 
loadings of chitosan: 0, 2.5, 5, 10, 15, and 20phr) was placed 
in separate bottles, and 10 mL of a standard solution was added 
to each bottle. Then, the bottles were covered with a paraffin 
film and kept at ambient temperature (25–30 °C) for 48 h. 
Subsequently, the resulting biocomposites were isolated using 
a filter paper and placed in an oven set at 40 °C to dry for 24 h, 
i.e., until a constant weight was obtained for each sample. The 
initial and equilibrium metal-ion concentrations were 
determined by absorbance measurement using atomic absorption 
spectroscopy (AAS) (PerkinElmer 3100). The effect of 
adsorbent dose on the uptake of Cu(II) ions from aqueous 
solution was also studied by varying the weight between 0.2 
and 0.4 g. All adsorption experiments were performed three 
times, and the average values were used for all calculations. 
The adsorption after 48 h was calculated using eqs 1 and 2

\[
\% \text{ of adsorption} = \frac{C_0 - C_i}{C_i} \times 100\% 
\]  

where \(C_0\) is the initial concentration (mg/L), \(C_i\) is the final 
concentration (mg/L), \(V\) is the volume (L) of solution, and \(W\) 
is the weight (g) of the absorbent used.

Desorption Experiment. To investigate the desorption of 
Cu(II) from the biocomposites CTS-t-ENR, the following 
method was carried out. After the adsorption took place, the 
biocomposites were dried at 60 °C and kept in a desiccator. 
These dried biocomposites were then placed in a beaker 
containing 10 mL of distilled water and covered with paraffin 
film for 60 h. Samples were withdrawn after 48 h, and the 
solution was analyzed using AAS. All desorption experiments 
were performed three times, and the average values were used 
for all calculations. The amount of Cu(II) release was 
calculated using eq 3.

\[
\% \text{ of amount release} = \frac{\text{the amount of Cu(II) released into the solution}}{\text{the initial amount of Cu(II) adsorbed}} \times 100\% 
\]  

Biodegradation Study in Soil Burial Test. Soil burial 
test was used to assess the biodegradability of the CTS-t-ENR 
biocomposites. Soil was standardized using garden soil filled 
into designated pots, which underwent a degradation period of 
a few weeks. The soil temperature was kept around 30 °C. One 
film of each chitosan loading was grouped according to 
the number of weeks. Grouped samples were weighed individually 
and buried within the soil in a stacking manner in different 
pots and taken out from the soil on a weekly basis. After that, 
the samples were withdrawn carefully, washed with distilled 
water, dried, and reweighed. The weight or mass loss of various 
degraded samples and reduction in the samples due to soil 
degradation were determined. Mass losses were calculated 
based on eq 4

\[
\text{percentage mass loss} = \frac{m_f - m_i}{m_i} \times 100\% 
\]  

where \(m_i\) is the mass before burial and \(m_f\) is the mass after 
burial.

RESULTS AND DISCUSSION
Effect of Chitosan Loading on Copper Adsorption. 
CTS is known to have a good Cu(II) affinity and adsorption 
capacity at around pH 5–5.5. Therefore, all of the trials were 
carried out at pH 5.2 to eliminate the effect of pH on the 
adsorption kinetics. The effect of CTS loading on Cu(II) ions adsorption by 
CTS-t-ENR biocomposites was investigated, and the results 
are presented in Figure 1. As seen from Figure 1, generally 
adsorption percentage and adsorption capacity would increase 
with an increase in CTS loading. The 0phrCTS-t-ENR 
biocomposite plays a vital role, whereby it can absorb about 
39.5% of Cu(II) ions. However, a slight decrease in adsorption 
was noted with 2.5phrCTS-t-ENR and 5phrCTS-t-ENR 
biocomposites. At higher loadings (10phrCTS-t-ENR, 
15phrCTS-t-ENR, and 20phrCTS-t-ENR), the adsorption 
properties are better than that of 0phrCTS-t-ENR. At 2.5phr 
and 5phr, the adsorption percentage and adsorption capacity 
are lower due to the lesser number of amino groups available 
for the uptake of Cu(II) ions. Each absorbent used in this
The study had different Cu(II) ion adsorption capacity values. The increase in the adsorption of Cu(II) ions value was merely dependent on the content of the amino group. Therefore, increasing CTS loading means more amino groups, and this contributes to more adsorption active sites available. Thus, this is one of the main reasons for the entrapment of CTS in a rubber matrix as more NH₂ groups were exposed on the surface. The entrapment enhances the interaction between CTS and the Cu(II) ions, and this actually prevents any tendency of CTS to agglomerate. With this, the availability of active binding sites on the CTS for adsorption of Cu(II) ions is also increased. In general, the biocomposites showed a lower adsorption capacity than CTS by itself.

Based on the scanning electron microscopy (SEM) image in Figure 2a,b, it is quite notable that the porosity is lesser in 2.5phrCTS-t-ENR than in the 15phrCTS-t-ENR biocomposite. Since the adsorption capacity is correlated to the number of binding sites of the amino group, more amino groups are exposed when the porosity is more. Therefore, most of the available amino groups would bind the Cu(II) ions, and from this point of view, the CTS-t-ENR biocomposites seem to be better absorbents than CTS itself. This indicates that the entrapment of CTS in the partially cross-linked ENR50 improves the adsorption capacity slightly better than any of its components used alone. The justification for this could be the influence of the three-dimensional structure, which is different for each individual component. The chelating group from CTS may alter the chelating combination and the interaction with metal complex. Thus, by combining CTS with ENR50, CTS actually altered its three-dimensional structure accordingly to enhance the contact with Cu(II) ions. Besides, CTS is also known to agglomerate or form a gel in an aqueous media, especially acidic media; therefore, the exposed site for the adsorption is also reduced in CTS itself and thus the capacity is also reduced.

This theory can be further explained using our model study. When the CTS beads were dried, they shrink severely. The dried biocomposites consist of void surrounding the trapped in a CTS material, as shown in Figures 2c and 4d. Therefore, when the water penetrates through the pores of the rubber matrices, they diffuse slowly along the aqueous pathways to the CTS. And since these CTS are able to swell, they will swell to the maximum to fill up the void or the space (domain) rubber (Figure 2c,d). This phenomenon is explained by the swelling capability of CTS in water. And when the Cu(II) ions are present in the solution, the ions penetrate slowly to the rubber matrices and reach the CTS. Therefore, the higher the CTS loading, the higher the adsorption possibility, due to more exposed CTS on the surfaces.

![Figure 1. Effect of chitosan loading on copper adsorption.](image1.png)

![Figure 2. SEM image of (a) 2.5phrCTS-t-ENR and (b) 15phrCTS-t-ENR. Schematic representation of (c) 15phrCTS-t-ENR biocomposites and (d) 20phrCTS-t-ENR biocomposites.](image2.png)
Based on these, it is very obvious that CTS contributes to the extraordinary effects to the biocomposites at higher loading (15 and 20phr). The voids created around the CTS also contributed to the extraordinary effect, whereby the Cu(II) ions have more pathways to be absorbed through the biocomposites, as explained earlier using our model study (Figure 2c,d).

Surface morphologies of the biocomposites clearly show the presence of pores with different sizes, and this may provide more adsorption sites for adsorbrates. Thus, the SEM image shown in Figure 4 clearly denotes that the biocomposite's adsorption property is enhanced due to the presence of the voids and the space between the entrapped CTS and the matrix. Besides, by entrapping the CTS in the rubber matrix, the specific surface area is also higher; therefore, the ability to capture the Cu(II) ions also increases. This is supported by Henry's law mode, in that the formation of new sites and pores in the polymer allows further adsorption.

**Effect of Chitosan Loading on the Copper Desorption.** The release of Cu(II) ions from CTS-t-ENR biocomposites is shown in Figure 3a. It is obvious from the plots (Figure 3a) that the Cu-ion release increased with CTS loading and decreased upon 20phr loading. It was found that CTS showed an almost negligible release of Cu(II) ions absorbed; therefore, the data are not presented here. Even though CTS itself has better swelling properties, the probability that it is unable to release Cu(II) ions is because of the very good adsorption capacity of CTS that it is unable to release the ions.

The 0phrCTS-t-ENR can release the Cu(II) ions slowly with only 0.45 mg/L, and this amount increases with 2.5, 5phr, and up to 15phr and decreases at 20phr loading. It is also clear from Figure 3a that the Cu(II)-ion release is highest in the 15phrCTS-t-ENR biocomposite compared to the other CTS-t-ENR biocomposites. The release from 15phrCTS-t-ENR biocomposite is about 2 times higher than that from 0phrCTS-t-ENR biocomposite. This is due to the hydrophobic nature of rubber. The rubber swells slowly in water; therefore, the release is very much slower and finally stops. In the 10phrCTS-t-ENR and 15phrCTS-t-ENR biocomposites, the Cu(II) ions are more likely to be surrounded by CTS, a hydrophilic compound that then swells better in water, resulting in a higher release of Cu(II) ions. The release rate of Cu(II) ions significantly increased with CTS loading.

It is well known that CTS has an excellent swelling property; therefore, increasing the CTS content in a rubber matrix increases the swelling ability. Therefore, the higher the CTS content, the better is the release of the Cu(II) ions, as the Cu(II) ions entrapped inside the biocomposites are high. The entrapped Cu(II) ions in the biocomposites can only be released when water starts to penetrate the network of the biocomposite. It will swell the biocomposites and dissolve the Cu ion absorbed earlier and then diffuse it to the surface. Here, the rubber plays a vital role whereby acting as a barrier. This rubber barrier slows down the adsorption process, again allowing the ions to be released to the surface. Thus, the release of Cu(II) ions increases the CTS content to a certain level.

In theory, the more ions are adsorbed, they should be able to release more. However, our finding is contradictory to this phenomenon. The amount of Cu(II) ions desorbed decreases drastically in the 20phrCTS-t-ENR biocomposite. This suggests that, as the CTS loading increases, adsorption would increase, but desorption decreases. This may be due to the more exposed CTS, as shown in our model (Figure 2d). During the biocomposite preparation, the rubber matrix cross-linked entraps the CTS. As the CTS loading reaches 20phr, the CTS are no longer fully trapped and some of it is exposed on the surface. Those CTS do not have a barrier like the entrapped CTS, and they hold back to the absorbed Cu(II) ions due to the nature of CTS. Therefore, for further analysis of desorption, 20phr is not taken into consideration.

To propose the kinetics and the mechanism of the slow release of the copper ions, the data were fitted to the kinetic equations such as zero-order rate, first-order rate, Higuchi, Ritger–Peppas equations. However, the data from 0 and 2.5phr could not be analyzed as the copper ions released were within 12 h, as shown in Figure 3b. An exception was observed with the composites having 5phr loading of CTS, where the relationship was not linear, which could be attributed to a decrease of the diffusion pathway due to low CTS loading.

**Table 1. Kinetic Mechanism of Copper (II)-Ion Release from CTS-t-ENR Composites**

| Chitosan loading (phr) | Zero order \( Q_t = Q_0 - k_0 t \) | First order \( \ln Q = \ln(Q_0) - k_1 t \) | Higuchi \( Q = k_2 t^{1/2} \) | Ritger–Peppas \( Q = k_3 t^n \) |
|-----------------------|-------------------------------|-----------------------------|------------------------|---------------------------|
| 5                     | 0.73                          | 0.69                        | 0.82                   | 0.88                      |
| 10                    | 0.95                          | 0.86                        | 0.98                   | 0.97                      |
| 15                    | 0.94                          | 0.84                        | 0.98                   | 0.97                      |

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The desorption results obtained were found to well fit the zero-order equation (amount of Cu ions released versus time). From Figure 3b as well as the regression parameters in Table 1, it is quite notable that a high correlation coefficient was acquired with all $R^2$ values close to agreement. These $R^2$ values were higher than that obtained with the first-order equation. These data strongly support that the diffusion of Cu-release mechanism from the CTS composites is nondependent on copper concentration.

When the desorption data obtained were fitted using the zero-order rate equation (logarithm amount of Cu released versus the square root of time), it is evident from Figure 3b as well as Table 1 that the plots are nonlinear and the regression values are low, proposing that the release kinetics did not follow first order. This indicates that the rate of Cu-ion release from the composites was nondependent on the amount of Cu available for release/diffusion from the composites.

In addition to the first-order equation, the data obtained also fit well with the Higuchi square-root equation, which is the amount of ion released versus the function of the square root of time. From Figure 3b as well as the regression parameters in Table 1, it is quite notable that a high correlation coefficient was obtained with 5, 10, and 15phr loadings, suggesting that the ion-release process is diffusion-controlled. Hence, the regression values also increased as the CTS loading increase. This is due to the increase in CTS content, which resulted in an increase in the diffusion path length of the ions. In addition, based on the data in Table 1, the $K_H$ value or the slope of the Higuchi’s curve for 15phr loading is greater than those of other loadings, indicating that the ion release was faster at this loading.

The copper (II)-ion release behavior was also fitted in the Ritger–Peppas equation (logarithm percentage of copper (II) ion versus the function of logarithm time). It was found that it fitted quite well into the equation with all of the regression values quite close to each other. The value of the release exponent ($n$) was found to be a function of the CTS loading, and it was found to increase as the CTS loading increases. The value of $(n)$ was found to be between 0.37 and 0.72, signifying that the copper (II)-ion release mechanism followed case II diffusion, whereby it corresponds to fickian diffusion release where the relative relaxation time of the polymer is much shorter than the characteristic diffusion time of water transport, which is controlled by a concentration gradient. This could be attributed to the high viscosity of the polymer and increase of strong entanglement of the bonds between the CTS and the rubber matrix, which increases the diffusion path length of the matrices as well as higher resistance to erosion by the dissolution medium.

The kinetic study of the copper (II)-ion release from the CTS–rubber biocomposite clearly supports that the driving force for the release of copper (II) ions is the penetration of the release medium. Therefore, contact of the biocomposites with water allows the latter to diffuse into the CTS through the rubber matrix. Thus, CTS swell and allow the ions to diffuse through the pores. Increasing the CTS content increases the porosity of the rubber and increases the release rate of the ions.

Biodegradation Study of the CTS-t-ENR Composite. Figure 4 shows the effect of CTS loading on the biodegradation property under different conditions. The 0phrCTS-t-ENR biocomposite shows a very slow degradation phase compared to the CTS-t-ENR biocomposite. It can be said that the hydrophobicity of ENR50 is the key reason for its resistance to microbial enzymatic systems. It is notable that for the first 3 weeks, the degradation is quite slow and a slight increase in weight percentage was noted from the 3rd to 4th week. However, biocomposites with higher loading of CTS (5, 10, and 15phr) show an increase in weight loss after the 8th week, indicating that the degradation is still faster in the CTS-t-ENR biocomposite. It is likely that CTS in the biocomposites allowed water adsorption and provided appropriate environments for microbial colonization and degradation of CTS, resulting in the breakdown of the biocomposite. Other means that play an important role are physical destruction due to the microorganisms and the biochemical effects of the extracellular materials produced by the micro-organic activity. Additionally, the percentage of degradation is affected by ecological factors such as humidity, temperature, and biological activity. Since CTS is hydrophilic, rain, moisture, and humidity can contribute to degradation. This is proven when we conducted the experiments under three different conditions, whereby the samples were placed under the tree, under the shade, and directly under the sun. Therefore, the degradation is much faster in amorphous domains than in crystalline domains, as water penetration is easier within a disordered network of polymer chains.24 The SEM micrograph shown in Figure 5 also suggests that the weight losses in the biocomposites are not due to phasing out of CTS but due to biodegradation.

This nature of our CTS-t-ENR biocomposite allows the copper ions that are trapped inside to be further released by the biodegradation method. With these data, we are able to deduce that the copper adsorption and desorption study can lead us to apply this biocomposite for slow-release matrices.

**CONCLUSIONS**

Chitosan was found to be a good absorbent, but it does not have a good desorption property. It was found that CTS-t-ENR biocomposites with 0phr loading have moderate adsorption and desorption properties. With the increase in chitosan loading, it was found that the adsorption of copper ion increases. However, the desorption property of the biocomposites happens to be different. The desorption property of the biocomposites decreases upon reaching 20phr of chitosan loading. The desorption or slow-release study indicates that the copper (II) ion can be released at a very slow and control phase, as proven by the kinetic study.

![Figure 4. Effect of CTS loading on biodegradation of the CTS-t-ENR biocomposite.](https://dx.doi.org/10.1021/acsomega.0c04081)
Based on the biodegradation study, it was found that biodegradation increases with chitosan loading. Therefore, upon discontinuation of the copper-ion release by the diffusion method, it will be continued by the biodegradation method. The CTS-t-ENR biocomposite shows a good barrier for controlling the release of copper (II) ions from the composites and easily degrading in soil. Thus, these composites with good controlled-release and swelling properties could be very useful in the agricultural field.

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The authors declare no competing financial interest.

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