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Preparation and Characterization of Ion Exchanger Based on Bacterial Cellulose for Heavy Metal Cation Removal

Sohair Farag[1], Hassan M. Ibrahim[1*], Ahmed Amr[1], Mohsen S. Asker[2] and Amira El-Shafai[1]

[1]Textile Research Division, National Research Centre, 33 El Bohouthst. (Former El Tahrir St.), Dokki, Giza, Egypt, P.O.12622
[2]Microbial Biotechnology Department, National Research Center, 33 El Bohouthst. (Former El Tahrir St.), Dokki, Giza, Egypt, P.O.12622

Bacterial cellulose was prepared in our laboratory by using agriculture wastes. Egyptian bacterial cellulose was isolated from rotten apple. Modification of the prepared bacterial cellulose vis esterification reaction was performed by using succinic anhydride to create active carboxyl groups to be used as ion exchanger. Heavy metal ions such as Cu (II), Zn (II) and Hg (II) ions were used for evaluation the ion exchanger power of the modified bacterial cellulose. The prepared ion exchanger was characterized by using FT-IR spectroscopy and scanning electron microscope (SEM) imaging before and after metal ion absorption. In addition, the absorption and desorption cycles of the ion exchanger were studied. The results shown that the maximum absorption capacity percent of the prepared exchanger for Cu (II), Zn (II) and Hg (II) ions were found to be 81.8, 79.5 and 78.1% respectively.

Keywords: Bacterial cellulose, Absorption capacities, Reusability, Egyptian bacteria and heavy metal cation.

Introduction

During recent years there are more attention and recommendation to use biological materials to remove and recover heavy metals [1], due to high quality performance and low cost of the materials [2-4]. As shown in our previous work that the environmental-biotechnology field developments shows that heavy metals can be removed from aqueous solution by some types of bacteria, fungi, algae or yeast via adsorption process [5]. Several bacteria were used to produce cellulose was reported in our previous work [6].

The prepared bacterial cellulose has similar molecular structure to the plant cellulose [7]. However, the main difference is that the obtained bacterial cellulose free from both lignin and hemicellulose [8, 9]. Bacterial cellulose was used in several applications due to it has high crystallinity, water absorption, mechanical properties and ultra-fine structure [7, 10-12].

The adsorption capability of ion exchanger is influenced by several factors such as specific surface area, porous structure, contact time and temperature, liquor ratio, concentration of adsorbent and pH's of the medium. We studied these factors in our previous studies [13-15]. Generation of carboxylic groups on bacterial cellulose represents ideal sites for metal ion chelation which appears in high adsorption efficiency and excellent recyclability adsorption [1, 16].

In the present study we synthesized bacterial cellulose from our laboratory by using our isolated Egyptian bacteria as carbon source in static culture as reported in our previous work [17]. Then the synthesized bacterial cellulose was modified via esterification resection with succinic

*Corresponding author e-mail: hmaibrahim@gmail.com , phone number: +201223453327
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anhydride to generate ion exchanger with free carboxylic groups. Finally, the modified bacterial cellulose was used as a bio sorbent for Zn^{2+}, Cu^{2+}, and Hg^{2+} from aqueous solutions. FT-IR spectra and SEM imaging were used to characterized the prepared bacterial cellulose and its efficiency as ion exchanger was evaluated by using adsorption and desorption of heavy metals at several cycles.

Materials and Methods

Materials

Bacterial cellulose was prepared by using isolated bacteria, treated molasses as carbon source at pH 6, temperature 35 ^{o}C for 5 days, extracted yeast as nitrogenous source, modified SH media in static culture. The produced bacterial cellulose was purified, lyophilized and finally freeze dried. Succinic anhydride, xylene and trimethylamine, acetate salts of copper, zinc and mercury. All chemicals and solvents were used at analytical grade and used without further treatment or purification.

Preparation of Carboxylated Bacterial Cellulose

Bacterial cellulose (1 g) was mixed with a succinic anhydride (3 g) and xylene (50 ml), triethylamine (4.2 ml) was added to from a solution. The solution was refluxed for 8 h. After that it left to cool at room temperature. The solution was filtered and the solid was washed thoroughly with acetone and water to remove unreacted succinic anhydride. The resulting light-yellow solid (1.8 g). was treated with sodium carbonate solution (0.01 mole/liter) for one hour under constant stirring and then filtered, the solid was washed with distilled water till the pH of the washing was neutral, then dried in oven at 60^{0}C [16, 18].

Adsorption of different metal cation by prepared exchanger

Typical adsorption experiment was conducted as follows: the stock solution of Cu^{2+} Zn^{2+} and Hg^{2+} (200 mg /L) was prepared by dissolving a certain amount of metal acetate in 1000 ml deionized water. 25 mg of the modified and unmodified bacterial cellulose was added to 25 ml metal cation solution under magnetic stirring at 120 rpm. pH adjustment was done by using buffer solution. After stirring, the samples were filtered through membrane and the residual metal cation concentration in the filtrate was determined by atomic adsorption spectrophotometer. The amount of metal ion adsorbs at equilibrium q_e (mg/g) equation (1), and the percentage removal efficiency (%R) were calculated according to equation (1):

$$q_e = \frac{(C_o - C_e)V}{W}$$
$$R\% = \frac{(C_o - C_e)\times 100\%}{C_o} \quad (1)$$

Where, C_o and C_e are the initial and equilibrium solution concentration of Cu^{2+}, Zn^{2+} and Hg^{2+} respectively. V is the volume of the solution and W (g) is the weight of the used bio sorbent and q_e

Desorption and Reusability of Prepared Exchanger

The regeneration of bacterial cellulose and functionalized BC were conducted using 0.1 mole NaCl solution as desorbing agent. The desorption lasted for 4hr under constant magnetic stirring (120 rpm) followed by repeatedly rinsing with deionized water to neutral pH.

Characterization of the Prepared Ion Exchanger

Carboxylic Content Degree of Succinylation

The carboxylic content of prepared exchanger was determined by the back titration method as follow [19]: 0.1 g of the sample was treated with 100 ml (0.01 mole /L) of NaOH standard solution by stirring at room temperature for one hour. Two drops of phenolphthalein indicator were added. The above solution was back titrated against 0.01 mole/liter HCl solution until the solution turned from pale pink to colorless. the carboxylic content was calculated by equation:

$$\mathrm{COOH\,(mmole/kg)} = \frac{V_{NaOH}\times C_{NaOH} - V_{HCl}\times C_{HCl}}{M} \quad (2)$$

Where V_{NaOH} and V_{HCl} are the volume of standard NaOH used and standard HCl consumed respectively, C_{NaOH} and C_{HCl} are the morality of NaOH and HCl respectively and M is the weight of the analyzed sample.

FT-IR spectrophotometer

Nexus 670 FTIR spectrophotometer (Leletco, USA) was used to verify the presence of carboxylic function groups on the surface of the bacterial cellulose.

Scanning Electron Microscope (SEM)

The morphology of the bio sorbent surface was seen by images before and after adsorption

of metal cation by using JOEL-JXA 840 electron probe micro-analyzer, Japan.

Results and Discussion

Ion Exchange Preparation

The protocol for synthesis of carboxylic groups in cellulose were done in our previous work [13, 17, 20-23]. The bacterial cellulose -OH groups reacted with succinic anhydride to form stable ester beside free -COOH end groups which accompanied by increasing of adsorption sites on its surface. We used tri ethylamine as a catalyst of the esterification reaction because it improves the consumption of the succinic anhydride up to 70% amount [24]. In addition, sodium carbonate was used to convert free -COOH groups to its sodium

Figure 2 shows FTIR spectroscopy of modified and unmodified bacterial cellulose. We obtain three major different peaks between the two spectra. In the modified bacterial cellulose, FTIR spectra shown peak at 1720 cm^{-1} corresponding to C=O stretching band of esters and carboxylic acid groups. The peak at 3468.89 cm^{-1} in the modified spectrum was associated to O-H stretching band of terminal acidic -COOH. Finally, there are increase and decrease in the absorption band intensities at 1170.58 and 1074.16 cm^{-1} for modified corresponding to C-O and C-O-C stretching band respectively [3, 17, 25]. So that FTIR spectra confirm that there are bacterial cellulose succinylation on at the OH groups of and the other dangle. The prepared ion exchangers contain (220 mmole -COOH /g sample) [3, 18, 26, 27].

Adsorption mechanism

We need to maintain the pH of adsorption solution constant for its adsorption mechanism illustration to obtain maximum adsorption. From our previous work [13, 17, 20-23, 28] normally; metal adsorbents exhibit a drastic decrease in metal affinity at low pH (less than 3) due to de-complexation of the metal cations in the stronger acidity medium.

Table 1 shows optimum values, pH's for Cu^{2+}, Zn^{2+} and Hg^{2+} respectively, adsorbance capacities for modified and unmodified bacterial cellulose and adsorption percentage.

The obtained data confirm that bacterial cellulose -COOH groups play an important role for the adsorption. The adsorption process at optimal condition, of 3 hours' time, room temperature and Liquor ratio (1:2). Every metal cation has its own pH where the pH of the adsorbed solution was detected in order to investigate its mechanism.

From our previous work [13, 17, 20-23], when the value of pH<4, there are electrostatic repulsive force between positive charges on both adsorbent and metal cation. At pH≥4 there are deprotonation of the adsorbent positive charged groups.

The prepared exchanger has higher adsorption capacity due to the attraction between bacterial cellulose negative charges and metal cations. Unmodified bacterial cellulose had affinity towards adsorbance of metal cation due to the presence of free OH groups which can chelate and form complex compound with the metal cation with percentage 63.6%, 61,3% and 60% for Cu^{2+}, Zn^{2+} and Hg^{2+}, respectively.

For modified bacterial cellulose the adsorbance percentage of metal cations removal from solution are 81.8% (Cu^{2+}), 79.5% (Zn^{2+}) and 78% (Hg^{2+}) respectively (as ionic radius decrease).

The amount of metal cation adsorbed resulting from incorporated carboxylic groups is higher than unmodified bacterial cellulose. Many research work deals about metal cation-poly electrolytes interaction [29-33]. All these studies concluded that one metal cation was chelated with to adjacent COO^- groups which lead to metal-poly electrolyte complex formation.

From the obtained results we expect that the metal cation-poly electrolyte interaction for Hg^{+2} differ from that for Cu^{+2} because differences in ionic radii (Hg^{+2} is more than Cu^{+2} in ionic radius). So the creation of -COOH groups on bacterial cellulose improve its binding with metal cation and its swelling by metal cations to increase metal cation uptake.

Reusability of Prepared Exchanger

For potential practical application, it is important to examine the possibility of desorbing the metal cations adsorbed on prepared exchanger and reusing the exchanger [24, 34]. The effect of five adsorption- desorption consecutive cycles the efficiency of the adsorption of Cu^{2+}, $Zn^{2+}$and Hg^{2+} on exchanger was studied. Table 2 shows the corresponding desorption efficiencies obtained, it was found that the Cu^{2+}, Zn^{2+} and Hg^{2+} adsorbed on modified bacterial cellulose were easily desorbed.

The desorption efficiency reached about 90% after the first cycle. We use mild desorbed agent

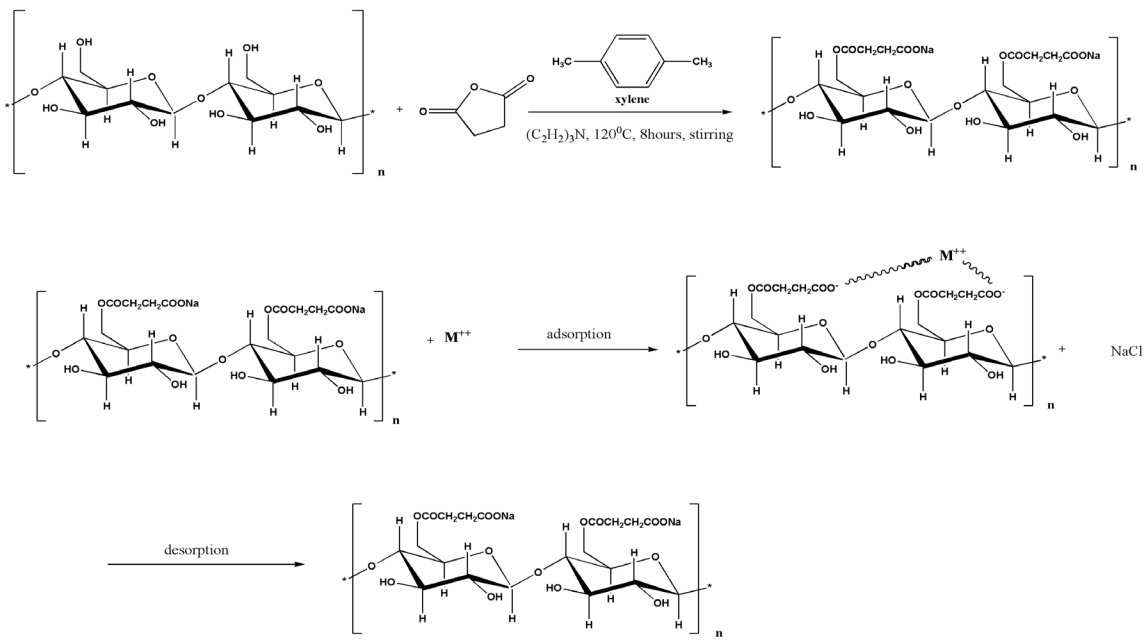

Fig. 1. Reaction mechanism, adsorption and desorption cycle

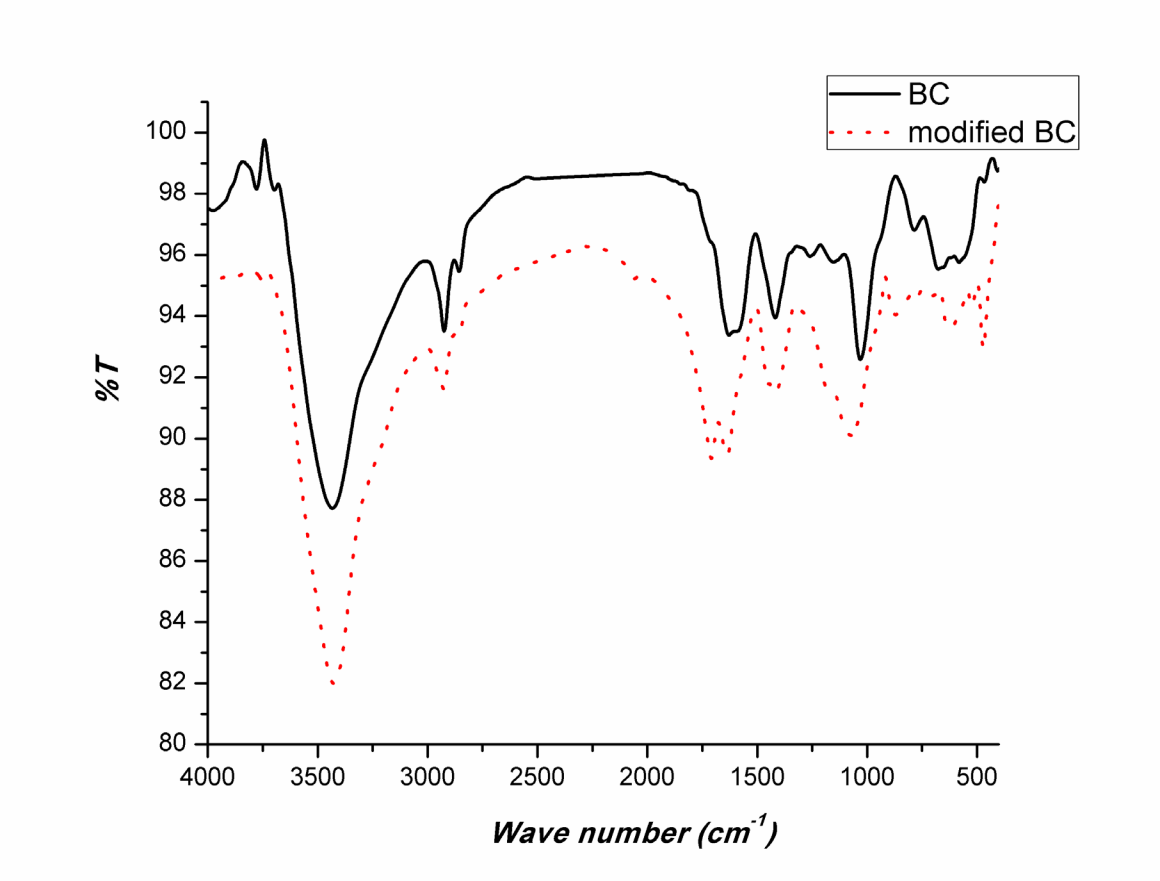

Fig. 2. FT IR of bacterial cellulose before and after carboxylation using succinic anhydride

NaCl to keep fine structure of bacterial cellulose or its active sites [35-37] and therefore it can be used as desorption solution. So that results of five adsorptions – desorption replications 4%, 1.71%, 1.04% was decrease in absorption capacity after five cycles. Therefore, it can be concluded that, the prepared exchanger can be reused without any significant loss in adsorption efficiency.

Surface morphology analysis by SEM

The SEM was recorded in order to provide further confirmation on the formation of metal cation complexes on bacterial cellulose surfaces; also to identify their position. Figure 3 shows the SEM of samples by scanning with a focused beam of electron. SEM micrographs of modified bacterial cellulose indicated in Figure (3a). The main structures of these samples display a homogeneous phase in both surface and cross-section and shows a relatively compact structure and smooth, indicating that -COOH groups almost homogenous cover the surface of bacterial cellulose, thus improving the metal adsorption capacity as well as the adsorption speed. After metal cation adsorption the morphology at the surface show more compact smoother and the metal cation were spreading on the bacterial cellulose surface (all the illuminated area in each image b, c and d which means that the carboxylic groups were in homogenous distribution on the bacterial cellulose surface.

In light of this approach, bacterial cellulose is reactive towards metal cation adsorption and has highest ion exchange efficiency after functionality. The modified bacterial cellulose sequestered more metal cation than a comparable unmodified bacterial cellulose, where the electrostatic attraction (between deprotonized carboxyl groups and metal cation) was the major removal mechanism.

Conclusion

In this study, ion exchanger based on bacterial cellulose was successfully synthesized by esterification of prepared bacterial cellulose. The formation of active sites on the surface of bacterial cellulose were substantiated by FTIR and SEM analysis. FTIR Spectroscopy confirmed the modification of bacterial cellulose. The prepared ion exchanger acquires (220 mmole -COOH/ bacterial cellulose) which are advantageous for the adsorption process. The maximum adsorption capacity for Cu^{2+}, Zn^{2+}, and Hg^{2+} cations were found to be 180, 175, 172 mg/g, respectively. Moreover, the prepared ion exchanger can be reused without having no significant loss of adsorption capability.

TABLE 1. Adsorption capacities and percentage of modified and unmodified bacterial cellulose

Metal Cation	PH	Adsorbance Capacities mg/g			
		Unmodified Bacterial Cellulose		Modified Bacterial Cellulose	
		Adsorbance (%)		Adsorbance (%)	
Cu^{2+}	4	140	63.6	180	81.8
Zn^{2+}	4	135	61.3	175	79.5
Hg^{2+}	4.5	132	60.0	172	78.1

TABLE 2. Reusability capacities and percentage of modified and unmodified bacterial cellulose

Metal ions	Zero cycle mg/g	1 Cycle	2 Cycle	3 Cycle	4 Cycle	5 Cycle	Decreasing (%)
Cu^{2+}	180	178	175	174	173	172.8	4%
Zn^{2+}	175	174	173	172.5	172.3	172	1.71%
Hg^{2+}	172	171.3	171.1	171	170.4	170.2	1.04%

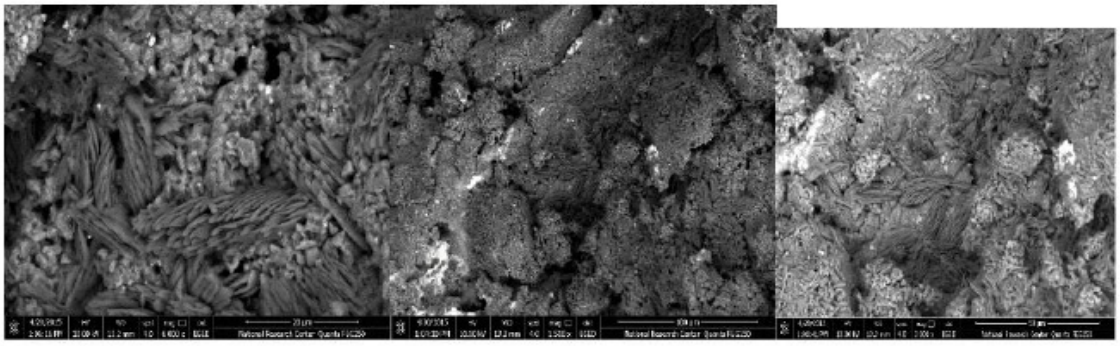

Fig. 3 (a) SEM of carboxylated bacterial cellulose before adsorption

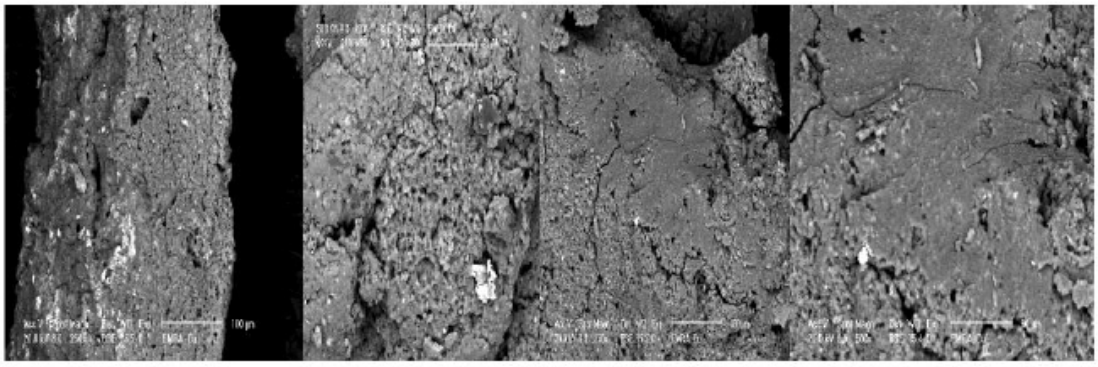

Fig. 3 (b) SEM of carboxylated bacterial cellulose after Cu^{++} adsorption

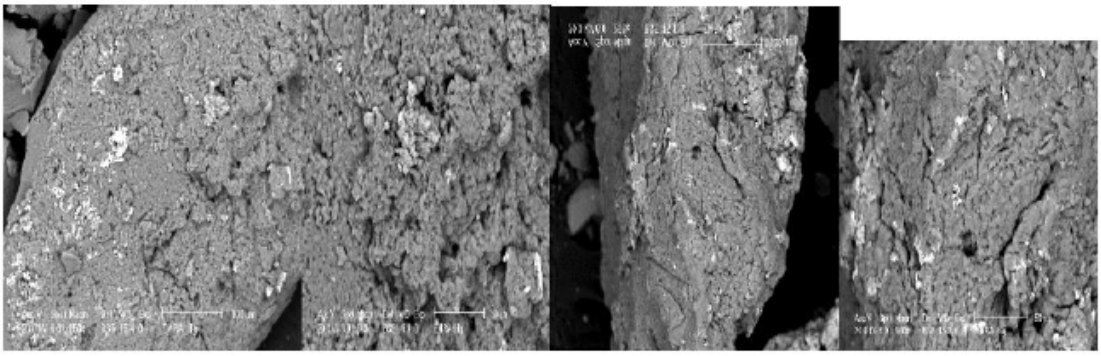

Fig. 3 (c) SEM of carboxylated bacterial cellulose after Hg^{++} adsorption

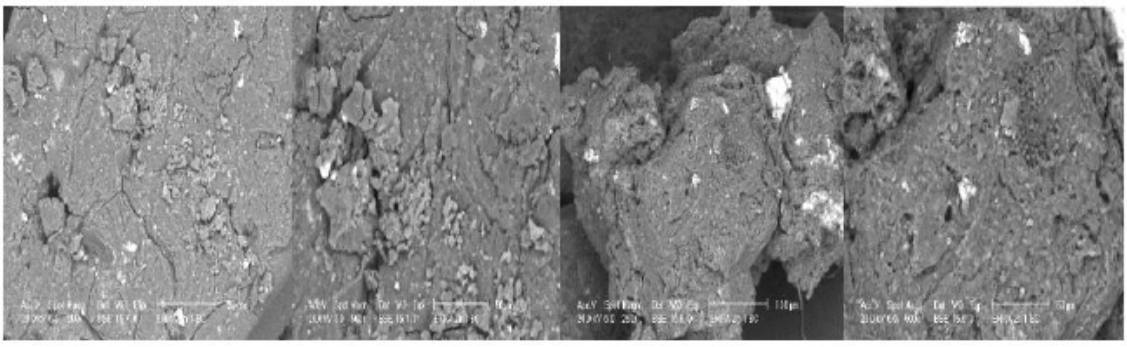

Fig. 3 (d) SEM of carboxylated bacterial cellulose after Zn^{++} adsorption

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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