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## Chapter

# New Ethylenediamine Crosslinked 2D-Cellulose Adsorbent for Nanoencapsulation Removal of Pb (II) and Cu (II) Heavy Metal Ions: Synthesis, Characterization Application, and RSM-Modeling

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## Abstract

The main objective of the present work is to elaborate on a new eco-friendly and efficient adsorbent designated for aquatic micropollutants removal. However, the synthesis of the Ethylenediamine Crosslinked 2D-Cellulose green adsorbent was carried out successfully, by partial grafting of benzyl entities onto hydroxyl groups of HEC, and crosslinking with ethylenediamine ED. Further, the new ethylenediamine crosslinked 2D-Cellulose was used as a biosorbent for nanoencapsulation removal of copper and lead heavy metal ions from aqueous solutions. The proposal chemical structures of unmodified and modified materials were confirmed using FTIR, XRD, TGA, and SEM-EDX analysis. Furthermore, many parameters of the optimization for Pb (II) and Cu (II) in terms of removal efficiency including pH, adsorbent amount, and contact time were optimized by response surface methodology with a Box–Behnken design. Based on the desirability optimization with three factors, the maximal removal was 99.52% and 97.5% for Pb(II) and Cu (II), respectively and was obtained at pH = 5.94, 22.2 mg as the optimal adsorbent amount, and 21.53 min as contact time.

**Keywords:** Cellulose, Ethylenediamine, Adsorption, Lead, Copper, Nanoencapsulation

## 1. Introduction

In the last few decades, the fast development of industrialization and urbanization caused a tremendous and exponential increase in the human population, where

the avoidance of the quality deterioration of water, air, and soil becomes the priority [1]. However, the pollution of aquatic environments by industrial effluents, in particular, water pollution by heavy metals, is the most serious problem due to their non-biodegradable properties, their persistence in the environmental media [2–6], toxicity to human health and ecosystems [7, 8]. Currently, the elimination of metal ions remains a major issue for environmental sustainability, where the greatest source of heavy metals contamination of wastewater is directly linked to anthropic activities, in particular industrial (textiles, rubber, leather, paper, plastic, coal, food, petrochemicals, etc.), agricultural (pesticides, forestry, etc.), pharmaceutical and hydrometallurgical activities [9–11]. Lead (Pb) is considered one of the main pollutants present in different components of the biosphere, where it accumulates through trophic chains or water intake [12]. In addition, Pb (II) ions are able, even at low concentrations, to causing severe central nervous system damage, kidney and immune system dysfunction in human beings, especially for children [8, 13–16]. Given its exceptional electrochemical aspect, copper occupies a prominent place in the international economy, where paving a large industrial area (energy, information, telecommunication, electronics, etc.), which is considered the second strategic raw material, in China, after oil [17, 18].

At the light of this, to decontaminate the industrial effluents from heavy metal ions, the efforts integrate the different separation techniques such as chemical precipitation [19, 20], membrane filtration [21, 22], flocculation and chemical coagulation [23, 24], biological treatment [25], ion exchange [26, 27], photocatalytic degradation [28], advanced oxidation [29], nanofiltration [30–32], and adsorption [33–38]. However, the adsorption process remains the most interesting and attractive technique due to its simplicity, ease of handling, high efficiency, ability to remove a large amount of organic and inorganic pollutants, and availability [39–42]. Faced with environmental constraints, the modern industrial policy requires well-defined qualities for basic adsorbent materials such as stability, retention capacity, low cost, biodegradability, etc. [43]. In this regard, cellulose, the most abundant, renewable, non-toxic, biodegradable, biocompatible, inexpensive, and environmentally friendly biopolymer in the world [44–48] has attracted increasing attention meeting ecological criteria [35, 49–51]. However, native cellulose showed a low adsorption capacity that indicating a low surface charge density. Thus, to improve its reactivity, it is necessary to reduce structurally related recalcitrance, where the exceptional chemical structure of cellulose, in particular the hydrogen bond type interactions at the supramolecular level, prevents its dissolution in almost all conventional solvents [52]. Another way to introduce new functionalities is to use cellulosic derivatives with more reactive accessibility. A good example of these derivatives is hydroxyethylcellulose (HEC), which makes it possible to obtain good solubility in an alkaline medium and water [53]. In addition, the reactivity of HEC is greater than that of cellulose because the density of the primary alcohol entities has increased [33], which gives the possibility of good control of the degree of substitution (DS), in particular for Williamson etherification of HEC grafted benzyl entities, where solubility has been successfully achieved and controlled in common solvents [54].

In this work, HEC was used as a water-soluble derivative of cellulose, where it was partially hydrophobized by introducing benzyl functionalities to decrease the average functionality of the reaction system, to avoid the 3D crosslinking in the following stage of the reaction, which ensures good accessibility of the pollutant load during the adsorption process, this ecological synthesis showed, in our previous article, that the degree of substitution does not exceed unity [33, 53–55]. Then, the benzoxyethylcellulose (BEC) polymer chains were crosslinked using ethylenediamine (ED) as a crosslinking agent and as a bidentate metal ion chelator,

especially for the removal of Pb (II) or Cd (II) [56–64]. Structural analyzes showed good agreement with the proposed structure of the new green adsorbent (BEC-ED). X-ray diffraction patterns and SEM confirmed the emergence of a new structural order of BEC-ED at the crystalline and morphological levels. However, the elemental surface profile of BEC-ED has been proven based on the EDS spectra. The effect of crosslinking on the ability to remove heavy metals from aquatic environments was studied as a function of physicochemical parameters (pH, nature of ions, contact time, initial concentration, etc.), which are optimized using the response surface methodology with the *Box–Behnken* design. To our knowledge, based on a review of the literature, the new green BEC-ED has never been described previously.

## 2. Materials and methods

### 2.1 Materials

HEC (DS  $\sim 1.5$ ) of 95% purity was purchased from HIMEDIA and it was purified by the dissolution-precipitation method in water-acetone solvents. Tetrahydrofuran (THF), ethylenediamine ED, thionyl chloride ( $\text{SOCl}_2$ ), DMSO, hydrochloric acid (HCl) 37%, and triethylamine ( $\text{Et}_3\text{N}$ ) were used as received from Sigma-Aldrich. Sodium hydroxide (NaOH) and Benzyl bromide were purchased from Merck. All other chemicals are analytical grade and were used as received without any further purification.

### 2.2 Methods

Fourier Transform Infrared spectroscopy (FTIR) spectra of the HEC, BEC, and BEC-ED samples were recorded on Shimadzu FTIR-8400S spectrometer using finely ground KBr pellets with 2% of the sample at a resolution of  $2\text{ cm}^{-1}$ . The measurements were performed over from  $4000$  to  $400\text{ cm}^{-1}$ , and averages of 40 scans were taken for each sample. The morphological SEM images of HEC, BEC, and BEC-ED were investigated using scanning electron microscopy (TESCAN VEGA 3 LM), with an accelerating voltage of 10 kV. Energy-dispersive X-ray spectra (EDS) were recorded to divulge the elemental profile presenting on unmodified and modified polymer surfaces. The sample crystal orders were evaluated using the X-ray diffraction technique and were obtained from EQUINOX 2000an X-ray Diffractometer, using copper radiation  $\text{CuK}\alpha$  ( $\lambda = 1.5418\text{ \AA}$ ), at an accelerating voltage of 40 kV and an operating current of 30 mA. All patterns are recorded in the range of  $2\theta$  ( $5^\circ$ – $35^\circ$ ). 0.25 g of each sample was pressed under 50 MPa to form pellets having an average of 25 mm in diameter. The thermal behavior of each sample was carried out on simultaneous DTA-TG Shimadzu DTG-60 apparatus. The amounts of the samples were between 8 and 12 mg and the interval of the temperature measurement was between room temperature and  $600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen flow. For all experiments, lead and copper ions concentrations were obtained by inductively coupled plasma-atomic emission spectroscopy on an ICP-AES (Iris Intrepid IIXDL ICP-AES).

#### 2.2.1 Preparation of BEC-ED

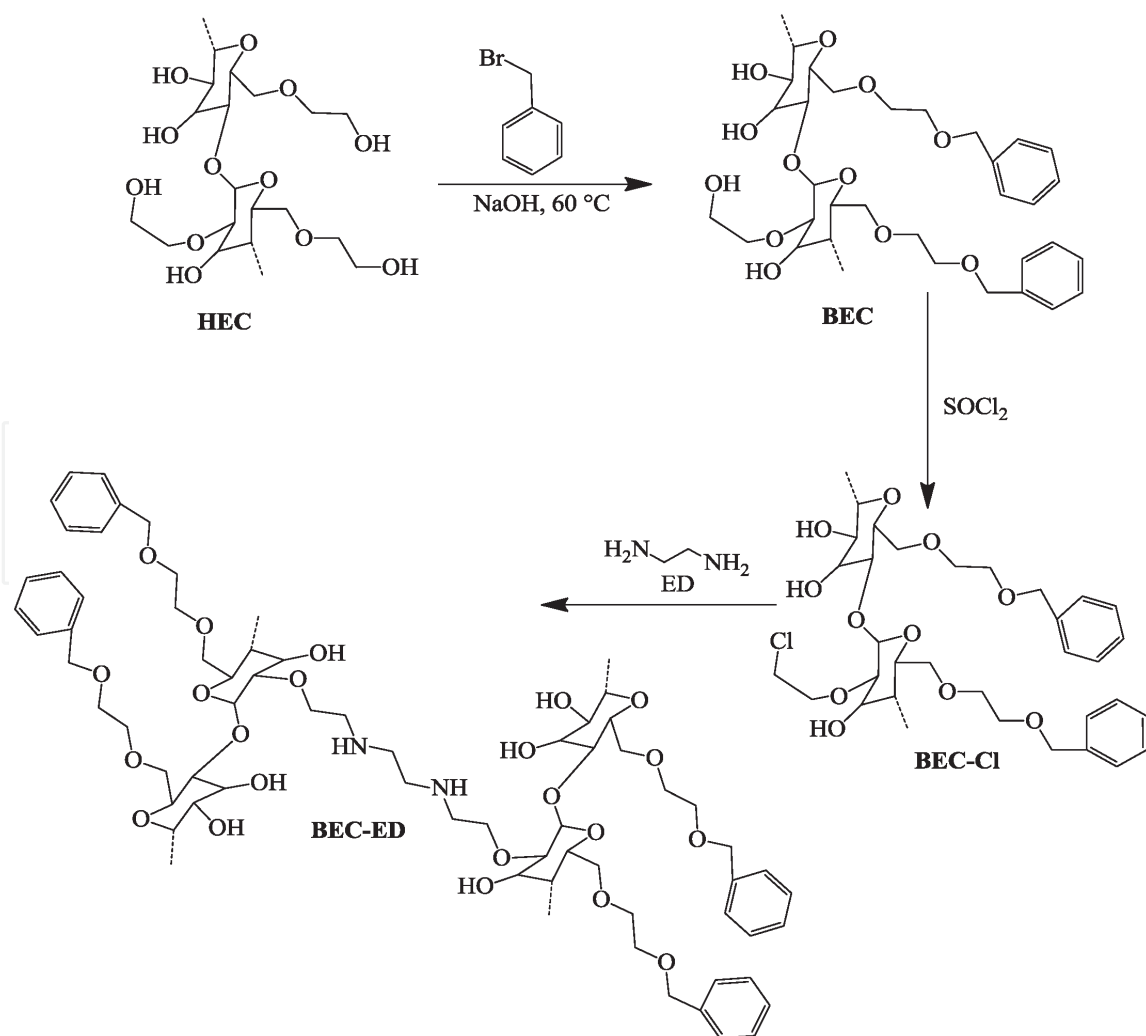
BEC was prepared according to the method described in our previous paper [54]. First, the crosslinking of BEC is carried out by passing through the chlorination of the free OH groups, as an intermediate step. Where, to 1 g (2.6 mmol) of the BEC dissolved in the minimum of DMSO, 0.38 ml (2.7 mmol) of ( $\text{Et}_3\text{N}$ ) and

0.40 ml (5.5 mmol) of Thionyl chloride  $\text{SOCl}_2$  were added dropwise. The reaction mixture was heated at  $70^\circ\text{C}$  for 2 h under stirring. The product is precipitated in water, filtered under vacuum, and then treated with 2% ammonia solution to neutral pH. Finally, the sample was washed frequently with water, filtered, and dried at  $70^\circ\text{C}$ . Ethylenediamine crosslinked BEC (BEC-ED) was carried out in THF at reflux for 4 h, where 1 g of BEC-Cl was reacted with ED in large excess (6 ml) using TEA as a capturing agent of HCl released. At the end of the reaction, the resulting product (white powder) was isolated by filtration under vacuum and frequently laved by distilled water to remove the ammonium salt and ED excess.

### 3. Results and discussions

#### 3.1 Synthesis and characterization

BEC-ED synthesis was performed after HEC hydrophobization (partial benzylation) to decrease the rate of crosslinking in bio-adsorbent. In addition, crosslinking was performed with ED to study the effect of graft grouping on the ability to remove heavy metals from aquatic environments. The originality of this work is summed up in the fact that this type of product has never been described previously in the literature. The reaction scheme for the synthesis of BEC-ED, as a novel heavy metal adsorbent in aquatic media, is shown in **Figure 1**. The



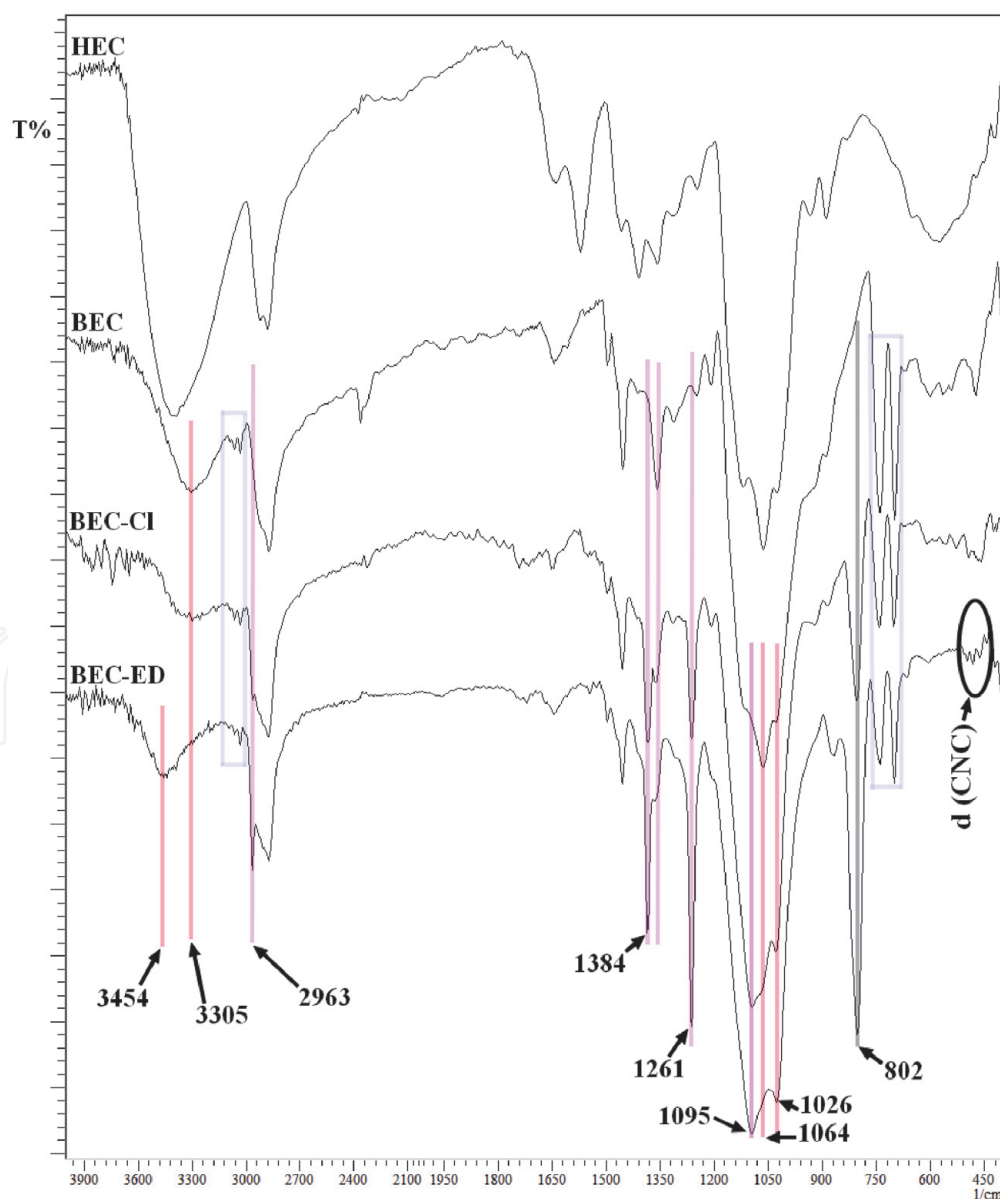
**Figure 1.**  
Reaction scheme of the preparation of BEC-ED.



crosslinking of BEC is carried out through the chlorination of the free OH groups, as an intermediate step, and then crosslinked by the ED in the THF using Triethylamine as the capturing agent of the released HCl to avoid the degradation of the cellulose chain under the effect of acid. However, the apparition of the white powder during the reaction indicating that the reaction of the crosslinking has been carried out successfully.

### 3.1.1 Structural analysis (FTIR)

FTIR spectra of HEC, BEC, BEC-Cl, and BEC-ED are given in **Figure 2**. The FTIR of unmodified HEC spectrum showed infrared absorption bands spotted at 1062, 1408, 1458, 2873, 2927, and 3412  $\text{cm}^{-1}$ . The absorption band at 3412  $\text{cm}^{-1}$  is attributed to O–H stretching vibration [65], and a medium absorption band located in the range of 2927 and 2873  $\text{cm}^{-1}$  corresponds to the C–H stretching vibration [66]. Moreover, the characteristic bands situated around 1408 and 1458  $\text{cm}^{-1}$  are attributed to C–H symmetric bending vibration in –CHOH and O–H plane deformation of a primary alcohol, respectively [55]. The absorption band of b-(1,4)



**Figure 2.**  
 The FTIR spectra of HEC, BEC, BEC-Cl and BEC-ED.

glycoside linkage was observed at  $887\text{ cm}^{-1}$  [67], and that of C–O–C stretching vibration in the glucopyranose at  $1062\text{ cm}^{-1}$  [68]. The absorption band at  $1120\text{ cm}^{-1}$  corresponds to the C–O asymmetric vibration [67]. It can be seen, in **Figure 2**, that the modification of HEC by the benzyl group is apparent with a decrease in the intensity of the peak at  $3347\text{ cm}^{-1}$  indicating a benzyl substitution of OH groups [69]. Indeed, the aromatic characteristic band elongations ( $=\text{C}-\text{H}$ ) are situated between  $3090$  and  $3033\text{ cm}^{-1}$  [70] and the aromatic C=Csp<sup>2</sup> elongation vibrations are located at  $1454\text{ cm}^{-1}$  [71]. In addition, the appearance of new absorption bands corresponding to the angular deformation (out of plane) of the monosubstituted aromatic C–H at around  $740\text{ cm}^{-1}$  [72], and the C=C aromatic angular deformation, situated at  $698\text{ cm}^{-1}$ , is a strong indication of the benzyl group incorporation on the HEC polymeric structure.

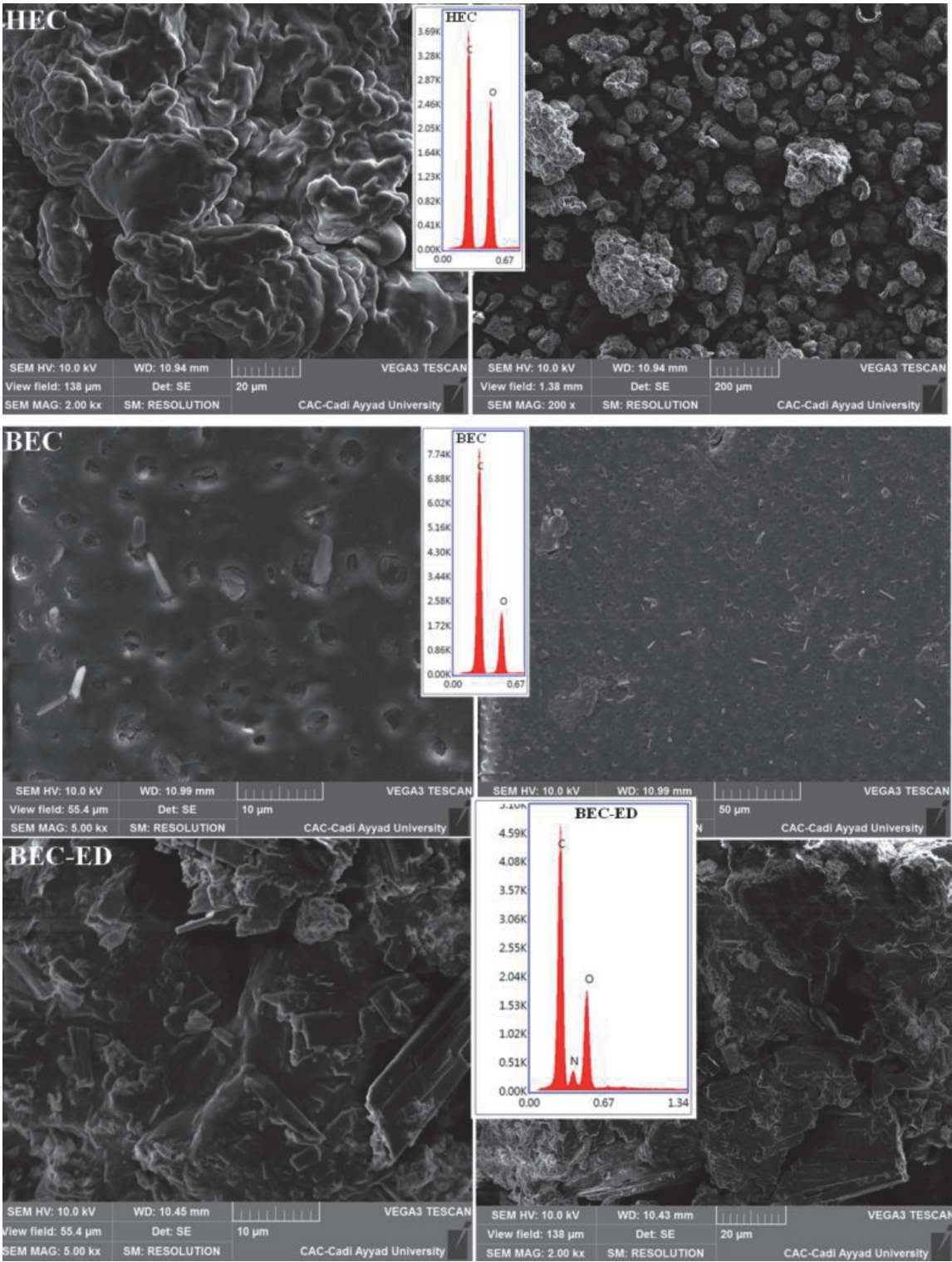
The comparison of FTIR spectra of unmodified BEC and chlorinated BEC (BEC-Cl) shows that the chlorination of BEC was carried out with success. Indeed, the new absorption band at  $802\text{ cm}^{-1}$ , attributed to the stretching of the carbon-chlorine bond C–Cl, is a strong indication that confirming the chlorination reaction. In addition, the decrease in band intensity at  $3305\text{ cm}^{-1}$  is due to the substitution of the hydroxyl group by chlorine, which confirms the success of the reaction [73, 74]. After BEC crosslinking, the appearance of the characteristic –NH– absorption band between  $3305\text{ cm}^{-1}$  and  $3454\text{ cm}^{-1}$  designates the incorporation of amino entities into the BEC structure. The increase in the density of –CH<sub>2</sub>– groups in the cellulosic skeleton is noticed through the increase in the intensity of the absorption band corresponding to the stretching vibrations of the methylene (–CH<sub>2</sub>) groups at  $2963\text{ cm}^{-1}$ . Furthermore, the ED crosslinking BEC is confirmed by the appearance of the different characteristic bands of the amino groups, which are located at  $1095\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$  corresponding to the NH and CN stretching vibrations, respectively [75]. Thus, the intense peak attributed to the out-of-plane strain of NH at  $802\text{ cm}^{-1}$  is very remarkable [75]. Also, the reduction in the intensity of the CO alcohol characteristic band around  $1200\text{ cm}^{-1}$  is a strong indication of the substitution of OH by NH of ED [76–78].

### 3.1.2 Scanning electron microscopy, energy-dispersive x-ray (SEM-EDS) spectroscopy

**Figure 3** shows SEM images of HEC, BEC, and BEC-ED. The resulted SEM images obtained for BEC showed homogenous, continuous, and microporous morphology, where pores diameter was estimated about  $(1\text{--}2)\text{ }\mu\text{m}$ , which is radically different from the HEC aggregation aspect and lamellar BEC-ED morphologies. Yet, the morphological character of BEC allows it to be considered as a good candidate for microporous adsorbent/membranes applications. However, the EDS spectra of HEC and BEC showed a very significant increase in the C/O ratio, which indicates that the benzyl entities are grafted successfully. The evidence of BEC crosslinking by ED is shown by the EDS spectrum corresponding to BEC-ED, where the peak corresponding to nitrogen is very noticeable. In addition, BEC-ED SEM images showed a Nanoscale laminated appearance, including a lamellar structure that occurs through hydrophobic interactions. Based on BEC-ED morphology results, a supramolecular structure is proposed and schematically illustrated in **Figure 4**.

### 3.1.3 X-ray diffraction (XRD)

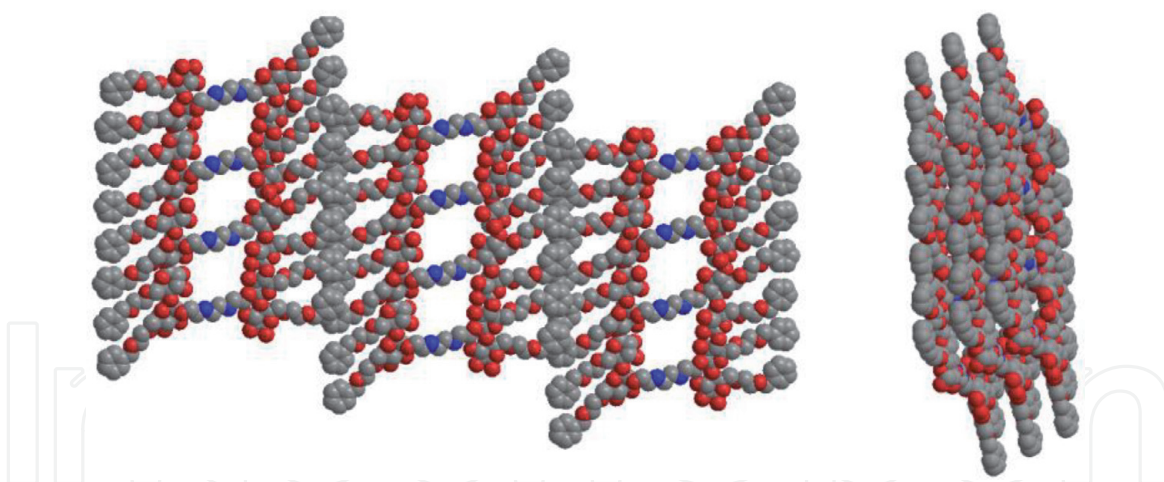
**Figure 5** shows the X-ray diffractograms of HEC, BEC, and modified BEC (BEC-ED) in the range of  $2\theta = 00^\circ$  to  $37^\circ$ . According to the diffractograms of the two polymers (HEC and BEC), the benzylation of HEC has practically no effect on the crystal behavior of HEC, except for a small shift of the maximum diffraction



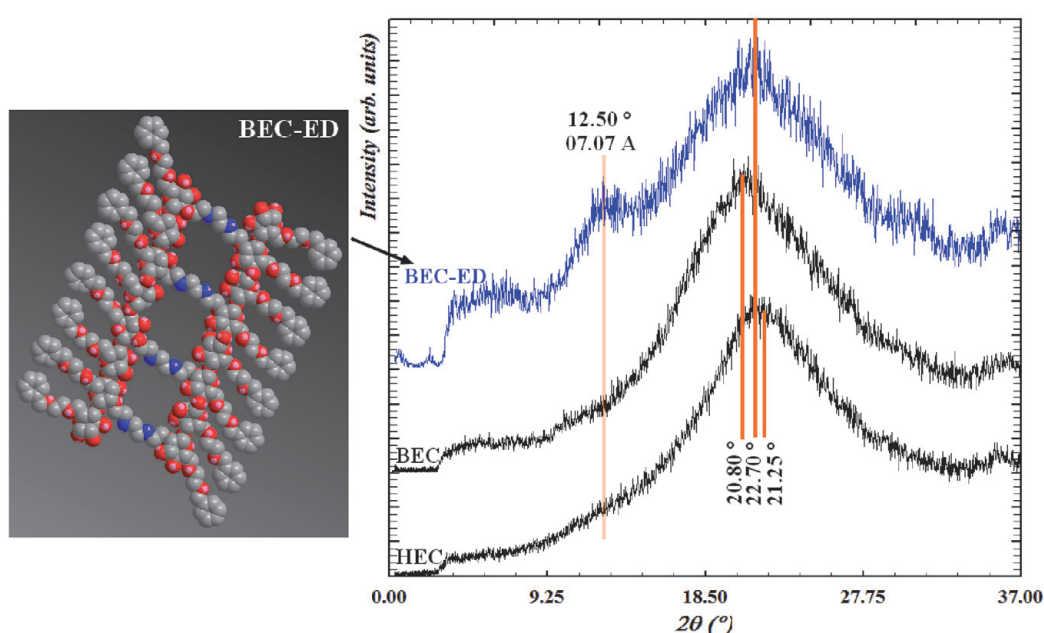
**Figure 3.**  
SEM images and EDS spectra of HEC, BEC and BEC-ED.

peak towards the low values of HEC,  $2\theta$  of  $21.25^\circ$  for HEC and  $20.80^\circ$  for BEC, but the predominance of the amorphous character is always considered. Though, the small decrease in  $2\theta$ , at this region, can be explained by the increase in the supra-molecular distance, between macromolecular chains, resulting from the insertion of benzyl entities. On the other hand, the diffractogram of the modified BEC sample (BEC-ED) showed, comparing to BEC, very remarkable and significant changes. Indeed, the crosslinking reaction of BEC generated a new crystalline order characterized by the apparition of a new peak towards  $2\theta = 12.50^\circ$ , which corresponds to a lattice distance of  $07.07 \text{ \AA}$  (Figure 5). The presence of a large domain with a





**Figure 4.**  
Supramolecular lamellar structure of BEC-ED.

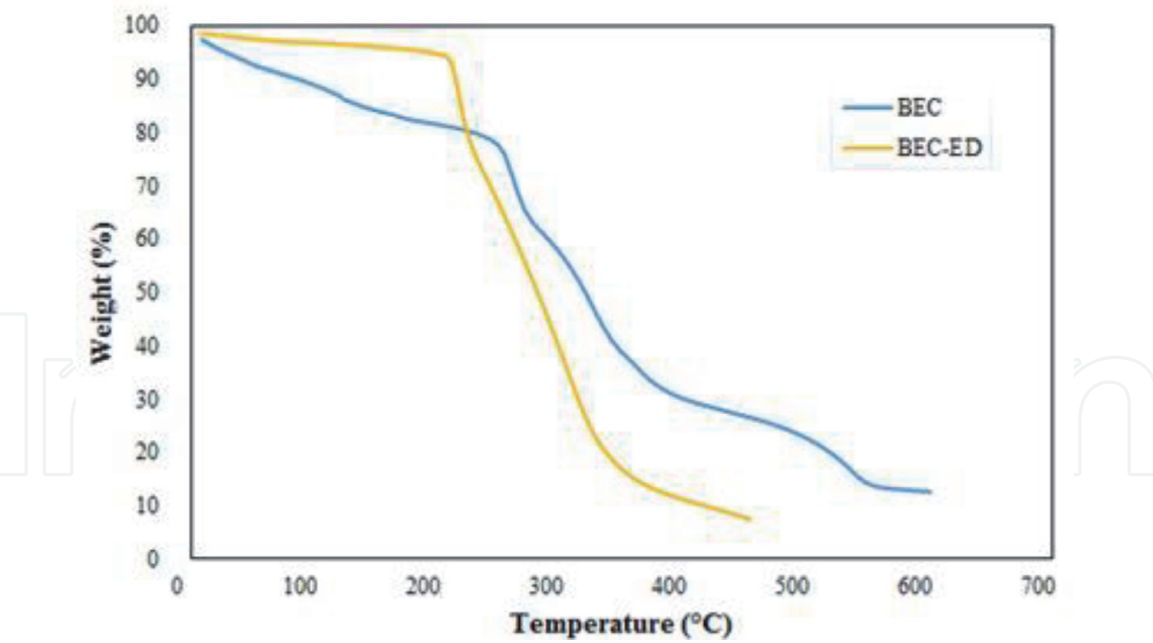


**Figure 5.**  
Supramolecular structure of BEC-ED and the XRD diffractograms of HEC, BEC and BEC-ED.

maximum at  $2\theta = 22.7^\circ$ , on the BEC-ED diffractogram, reveals its amorphous character. Therefore, a semi-crystalline appearance of BEC-ED can be suggested.

#### 3.1.4 Thermogravimetric analysis (TGA)

Thermogravimetric makes it possible to follow, as a function of temperature, the weight loss evolution of each sample, mainly caused by dehydration or/and by the decomposition of the organic matter it contains. The thermal stability of BEC-ED comparing to BEC is studied basing on the TGA thermograms shown in **Figure 6**. The thermal behavior of BEC shows two stages of thermal decomposition, the first one is observed between 35 and 250°C attributed to the solvents and adsorbed water vaporization [79]. The strong weight loss (70%) corresponds to the degradation of the grafted entities and the cellulose backbone is observed in the temperature range of 250–600°C. For BEC-ED, no thermal event was observed below 250°C, indicating the absence of traces of solvents. The thermal decomposition of BEC-ED is noticed from 250°C up to 450°C with a mass loss of 90%. In addition, a low degradation of the thermal stability of BEC-ED compared to BEC has been noted,



**Figure 6.**  
TGA thermogram profiles of BEC and BEC-ED.

Variables	Factors	Unit	Level 1 (−1)	Level 2 (0)	Level 3 (1)
X <sub>1</sub>	Ph	—	4.5	6	7.5
X <sub>2</sub>	Adsorbent amount	mg	10	20	30
X <sub>3</sub>	Contact time	min	5	17.5	30

**Table 1.**  
Coded and actual variables and their levels.

and this is possibly due to the decrease of hydrogen interaction density and their replacement by hydrophobic interactions, and the supramolecular separation of the polymer chains caused by grafted ethylenediamine (ED).

**3.2 Response surface methodology (RSM) modeling procedure**

In the current work, is focused on *3-level Box–Behnken design* (BBD) in response surface methodology for seeking the optimal conditions for the removal efficiency of Cu(II) and Pb(II) onto BEC-ED. The three variables affecting the current process are pH at 4.5, 6.0, and 7.5, contact time at 5, 17.5, and 30 min, and adsorbent amount at 10, 20 and 30 mg. The complete design consisted of three different levels (−1, 0, and + 1) and 3-variable (pH—X<sub>1</sub>, Adsorbent amount —X<sub>2</sub>, and contact time —X<sub>3</sub>). The layout of the factorial design is shown in **Table 1**. A total of 17 experiments were used in this study to evaluate the effects of the three input variables on Pb(II) and Cu(II) removal efficiency. The full picture of experiments with their responses (Pb(II) and Cu(II) removals) are tabulated in **Tables 2 and 3**, respectively.

The analysis of variance (ANOVA) was applied to the experimental runs, and then the results of the Box–Behnken design table are calculated and fitted by a suitable polynomial equation. According to the model’s evaluation in **Tables 4 and 5**, which focuses on maximum R<sup>2</sup>, predicted R<sup>2</sup>, and adjusted R<sup>2</sup>, the quadratic polynomial (Eq. (1)) model was chosen and well-fitted for all three independent parameters and responses (Cu(II) and Pb(II) removal efficiency).

	Factor 1	Factor 2	Factor 3	Response 1	Response 2
Run	X <sub>1</sub> :pH	X <sub>2</sub> :Adsorbent amount	X <sub>3</sub> :Contact time	Pb removal	Cu removal
		Mg	min	%	%
1	0	0	0	95.64	91.21
2	1	-1	0	40.27	43.24
3	-1	1	0	61.85	57.57
4	0	0	0	96.41	93.32
5	-1	0	-1	43.53	45.92
6	-1	-1	0	42.85	39.84
7	0	0	0	96.23	94.78
8	0	1	-1	69.08	73.12
9	1	0	-1	42.82	51.48
10	0	1	1	92.42	91.37
11	1	1	0	62.32	61.76
12	0	-1	1	68.34	62.28
13	-1	0	1	67.24	68.84
14	0	0	0	94.86	94.81
15	0	-1	-1	47.17	49.53
16	0	0	0	93.81	91.76
17	1	0	1	64.87	65.67

**Table 2.**  
The BBD matrix design with three independent factors and the corresponding experimental results.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7460.88	9	828.99	730.00	< 0.0001	Significant
A-pH	3.37	1	3.37	2.96	0.1288	
B-Amount	947.00	1	947.00	833.92	< 0.0001	
C-Time	1018.58	1	1018.58	896.96	< 0.0001	
AB	2.33	1	2.33	2.05	0.1955	
AC	0.6889	1	0.6889	0.6066	0.4616	
BC	1.18	1	1.18	1.04	0.3425	
A <sup>2</sup>	3566.13	1	3566.13	3140.31	< 0.0001	
B <sup>2</sup>	880.99	1	880.99	775.80	< 0.0001	
C <sup>2</sup>	573.67	1	573.67	505.17	< 0.0001	
Residual	7.95	7	1.14			
Lack of Fit	3.36	3	1.12	0.9779	0.4866	Not significant
Pure Error	4.59	4	1.15			
Cor Total	7468.83	16				

**Table 3.**  
ANOVA analyses of the quadratic model and determination coefficients for Pb(II) adsorption efficiency.

Source	Std. Dev.	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	PRESS	
Linear	20.57	0.2636	0.0937	−0.1046	8249.92	
2FI	23.44	0.2642	−0.1773	−0.9645	14672.20	
Quadratic	1.07	0.9989	0.9976	0.9918	60.98	Suggested
Cubic	1.07	0.9994	0.9975		*	Aliased

*\*Case(s) with leverage of 1.0000: PRESS statistic not defined.*

**Table 4.**  
 Model summary statistics Pb(II).

Source	Std. Dev.	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	PRESS	
Linear	19.32	0.2466	0.0728	−0.1445	7370.22	
2FI	21.97	0.2508	−0.1987	−1.0514	13210.51	
Quadratic	2.73	0.9919	0.9815	0.8955	672.91	Suggested
Cubic	1.67	0.9983	0.9931		*	Aliased

*\*Case(s) with leverage of 1.0000: PRESS statistic not defined.*

**Table 5.**  
 Model summary statistics Cu(II).

Therefore, the predictive polynomial quadratic response model can be described as the following equation (Eq. (1)) [80]:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^n \sum_{i>1}^n \beta_{ij} X_i X_j \tag{1}$$

Where Y is the predicted response, β0 and βi are the intercept coefficient, and the linear coefficient respectively, βii and βij are the quadratic and the interaction coefficients, respectively, while Xi and Xj represent the coded values of the independent variables.

An ANOVA analysis for Cu (II) and Pb (II) removals was performed, and the results are presented in **Tables 3** and **6**, respectively. According to ANOVA analysis, the results obtained showed that the F and P-values less than 1000 and 0.0500, respectively. This confirmed that the model terms are significant. While **Lack of Fit F-value** in the ANOVA tables introduces an insignificant error with regard to the pure error. The response for Cu(II) and Pb(II) removal efficiency was determined with real factors by the following expressions (Eqs. (2) and (3)):

$$\begin{aligned}
 Pb(II) \text{ Removal} = & -480.655 + 154.152 * pH + 6.49305 * Amount + 3.56334 * Time \\
 & + 0.0508333 * pH * Amount + -0.0221333 * pH * Time + 0.00434 * Amount * Time \\
 & + -12.9344 * pH^2 + -0.14465 * Adsorbent amount^2 + -0.074704 * Time^2
 \end{aligned}
 \tag{2}$$

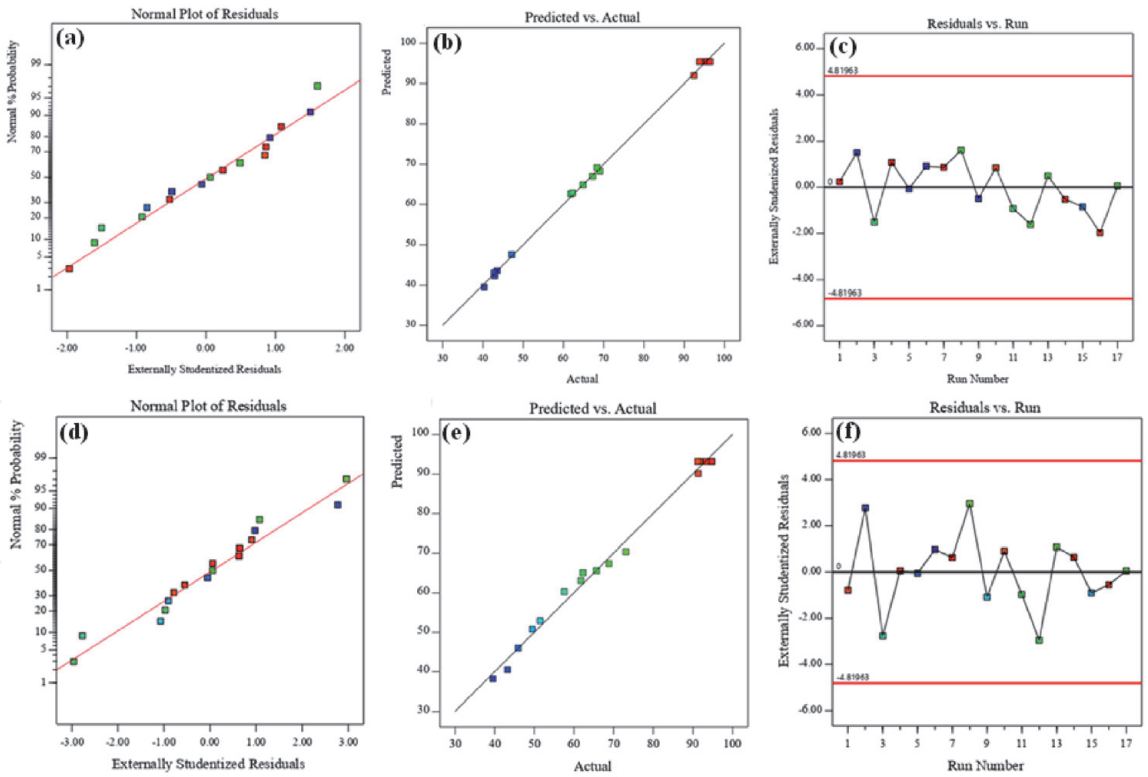
$$\begin{aligned}
 Cu(II) \text{ Removal} = & -462.971 + 146.053 * pH + 7.18408 * Amount + 3.02441 * Time \\
 & + 0.00816667 * pH * Amount + -0.1164 * pH * Time + 0.011 * Amount * Time + \\
 & -11.9436 * pH^2 + -0.157755 * Amount^2 + -0.0532832 * Time^2
 \end{aligned}
 \tag{3}$$

Statistical diagnostics test is an excellent and effective tool for confirming the model presented. These diagnostic plots are given in **Figure 7**. By classifying the



Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6387.74	9	709.75	95.35	< 0.0001	Significant
A-pH	13.21	1	13.21	1.77	0.2245	
B-Amount	995.25	1	995.25	133.71	< 0.0001	
C-Time	579.87	1	579.87	77.90	< 0.0001	
AB	0.0600	1	0.0600	0.0081	0.9310	
AC	19.05	1	19.05	2.56	0.1536	
BC	7.56	1	7.56	1.02	0.3470	
A <sup>2</sup>	3040.67	1	3040.67	408.51	< 0.0001	
B <sup>2</sup>	1047.86	1	1047.86	140.78	< 0.0001	
C <sup>2</sup>	291.85	1	291.85	39.21	0.0004	
Residual	52.10	7	7.44			
Lack of Fit	40.97	3	13.66	4.91	0.0792	Not significant
Pure Error	11.13	4	2.78			
Cor Total	6439.84	16				

**Table 6.**  
ANOVA analyses of the quadratic model and determination coefficients for Cu(II) adsorption efficiency.



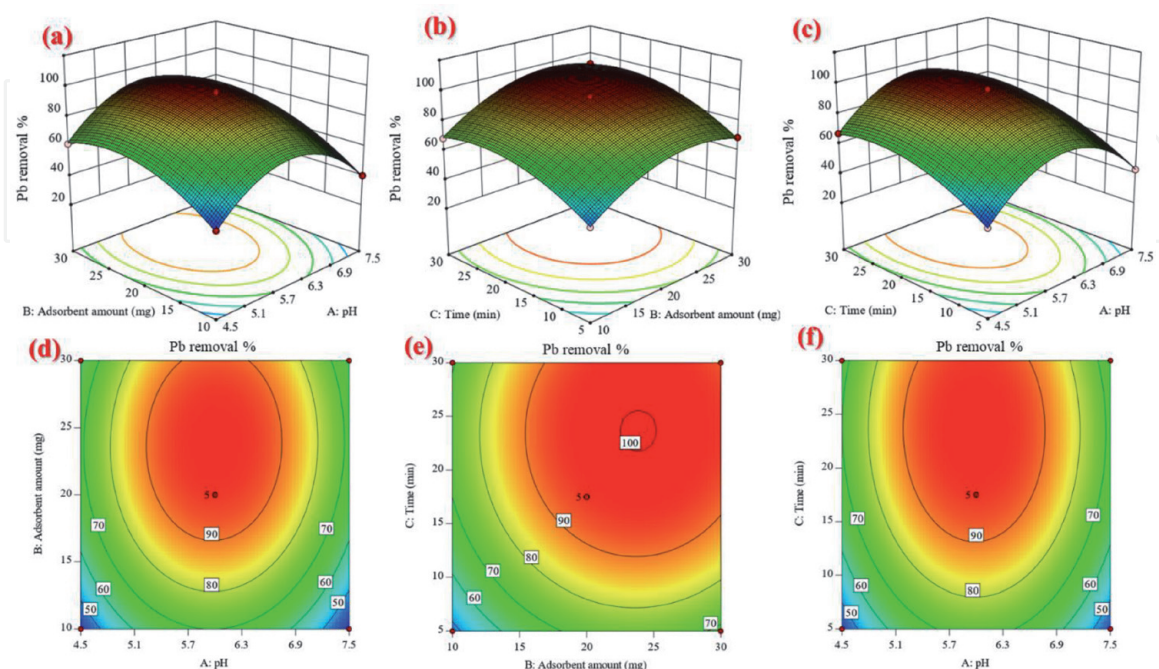
**Figure 7.**  
Diagnostic plots for adsorption of Pb(II): Probability plot for the studentized residuals (a), comparison between actual and predicted values (b), plot of the externally studentized residuals vs. experimental run number (c), diagnostic plots for adsorption of Cu(II): Probability plot for the studentized residuals (d), comparison between actual and predicted values (e), plot of the externally studentized residuals vs. experimental run number (f).

proportion of normal probability in terms of residuals, it can be observed that the datum-points are approximately straight-line (**Figure 7a** and **d**). Into the other diagnostic plots, the actual responses were compared to their residuals based on

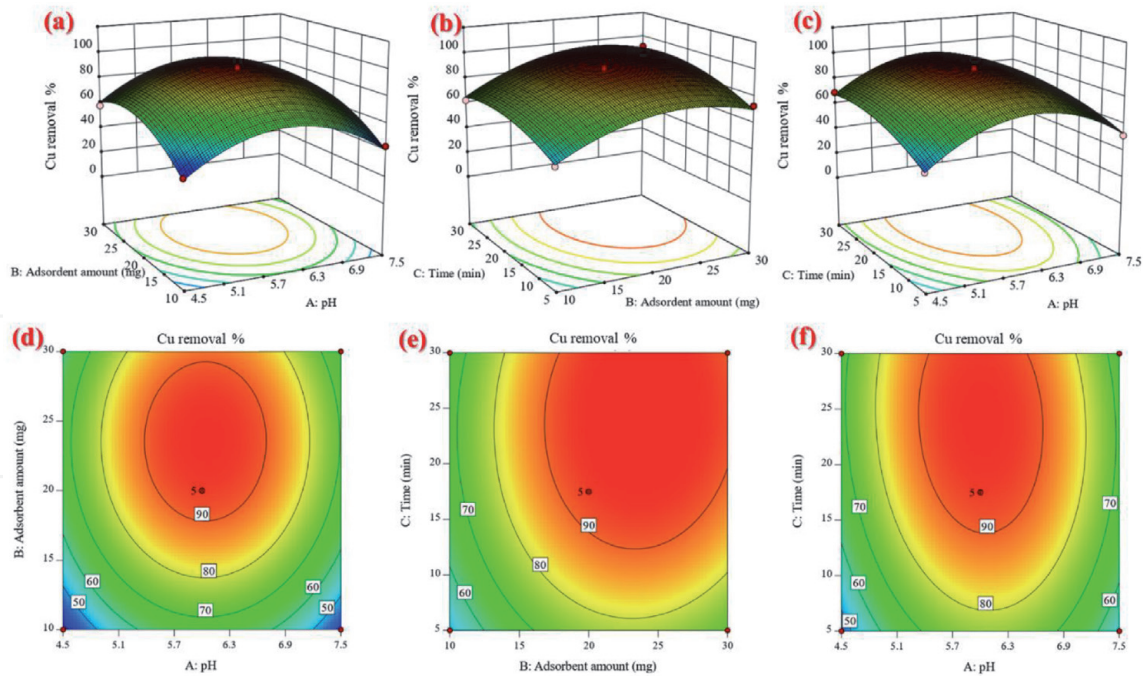
predicted responses, suggesting that the quadratic model was required to predict removal efficiency in the experimental parameters (**Figure 7b** and **d**). In addition, as shown in the plot (**Figure 7c** and **f**) the data showed a good homogeneity. In **Figure 7**, the dispersion of the residuals is dispersed randomly about  $\pm 5$ , confirming that the results are coherent with the model. In the other diagnostic plots, actual responses were compared to their residues based on predicted responses, implying that the quadratic model was necessary to predict removal efficiency in experimental parameters.

By employing the RSM method, the evaluated models (Eqs. (2) and (3)) are used to design the 3-D graphs and find the optimal conditions for Pb (II) and Cu(II) removal efficiency. It can be seen from **Figures 8** and **9** that the retention of Pb(II) and Cu(II) ions onto BEC-ED increases with increases of the pH solution. The removal efficiency reached a maximum of around 6. When the pH is higher than 6 or lower than 5 the adsorption decreased rapidly. This could be explained by that in the acidic environment, the active groups responsible for the adsorption process exist mainly in the  $\text{NH}_3^+$  form, and they prevent the retention of Pb (II) and Cu(I) ions on the amino groups of BEC. When the pH increases from 2 to 5, the active sites of the chelator become in the form of free  $\text{NH}_2$  amines, which facilitate chelation on Pb(II) [60]. In addition, at high pH, the formation of lead and copper hydroxides (**Figure 10**) limits their adsorption on the BEC-ED surface, and as shown in **Figures 8** and **9**, at high pHs, the removal efficiency of Pb(II) and Cu(II) ions is significantly diminished. Contact time was also examined and as given in **Figures 8** and **9**. The results of the retention of Pb(II) and Cu(II) onto BEC-ED revealed that the maximum adsorption equilibrium can be achieved rapidly around 16 min.

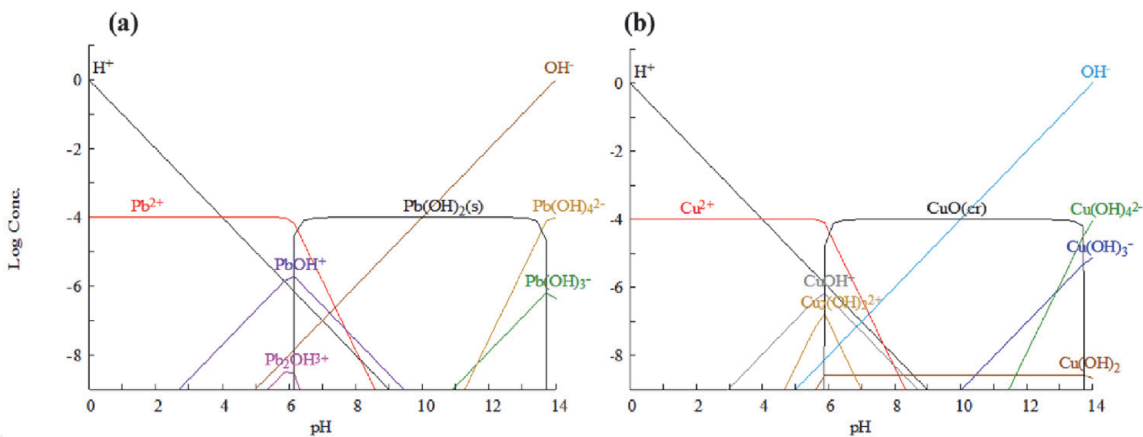
In conclusion, based on the desirability optimization with three factors, the best removal efficiency was 99.52% and 97.5% for Pb(II) and Cu(II), respectively and was obtained at pH: 5.94, adsorbent amount: 22.2 mg, and contact time: 21.53 min (**Figure 11**).



**Figure 8.**  
 (a, b and c) 3D response surface plot and, (d, e and f) contour plot for the effect of factors on the Pb(II) removal efficiency.



**Figure 9.** (a, b, and c) 3D response surface plot and, (d, e and f) contour plot for the effect of factors on the Cu(II) removal efficiency.

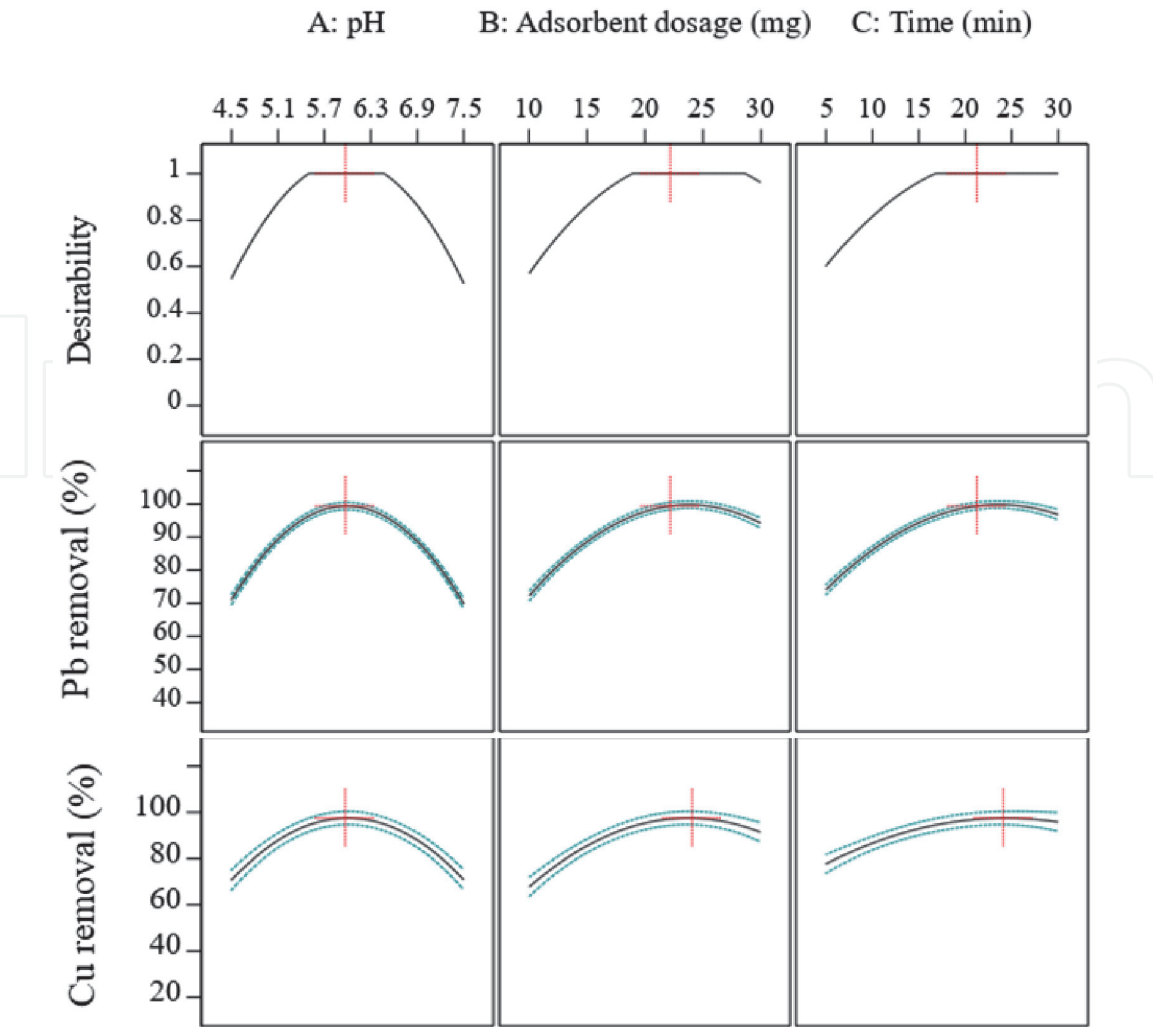


**Figure 10.** Speciation diagram of lead (a) and copper (b) as a function of pH in ultrapure water, determined by the hydra/medusa program [81].

### 3.3 Equilibrium isotherms

Adsorption isotherms for lead and copper were made by carrying out batch adsorption studies. Lead and copper adsorption was studied onto BEC-ED in a large concentration range (from 15 to 250 mg/L), to better model the retention mechanisms. The adsorption experiments were performed at room temperature by using a mass of adsorbent 22.2 mg with 50 mL of the aqueous solution, at pH 5.94 and contact time 21.53 min. The quantity of the lead and copper ions adsorbed onto the BEC-ED at equilibrium,  $q_e$  (mg/g), and the adsorption percentage was calculated by the following Equations [82]:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (4)$$



**Figure 11.** Desirability approach function optimization for Pb(II) and Cu(II) in terms of removal efficiency (%) and desirability.

$$\%Adsorption = \left(1 - \frac{C_e}{C_0}\right) \times 100 \tag{5}$$

Where,  $C_0$  and  $C_e$  are the metal ion initial concentration and concentration at equilibrium (mg/L), respectively.  $V$  is the volume of solution (L) and  $m$  is the adsorbent amount (g).

The adsorption isotherms of Cu(II) and Pb(II) on BEC-ED were modeled using the Freundlich (Eq. (6)) [83] and Langmuir (Eq. (7)) [84] models equations:

$$q_e = K_F C_e^{1/n} \tag{6}$$

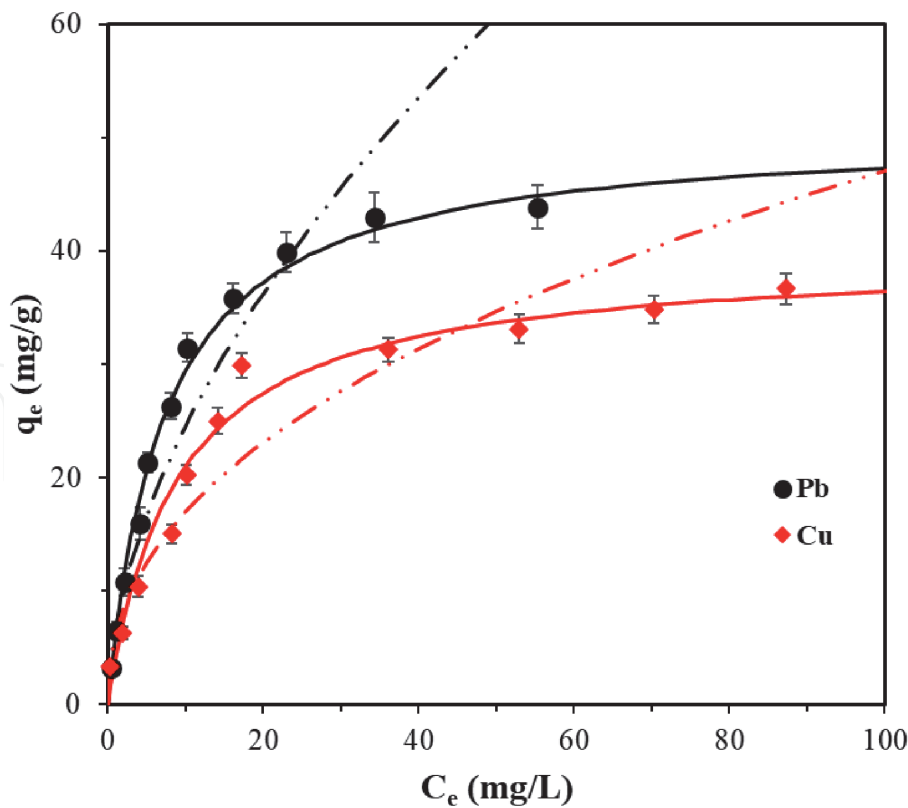
Where,  $n$  and  $K_F$  are Freundlich constants represent the heterogeneity index, and the adsorption coefficient, respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L q_m} \tag{7}$$

Where,  $K_L$  (L/mg) and  $q_m$  (mg/g) are the Langmuir constant and the maximum adsorption capacity, respectively.

The equilibrium isotherm obtained for lead and copper adsorption on BEC-ED is shown in **Figure 12**. Lead adsorption was greater than that of copper 43.85 mg/g. This could be explained by the higher reactivity of lead than copper, which can have





**Figure 12.** Equilibrium isotherms for Pb and Cu adsorption on BEC-ED (solid lines and dash-dotted represent Langmuir and Freundlich fitting, respectively).

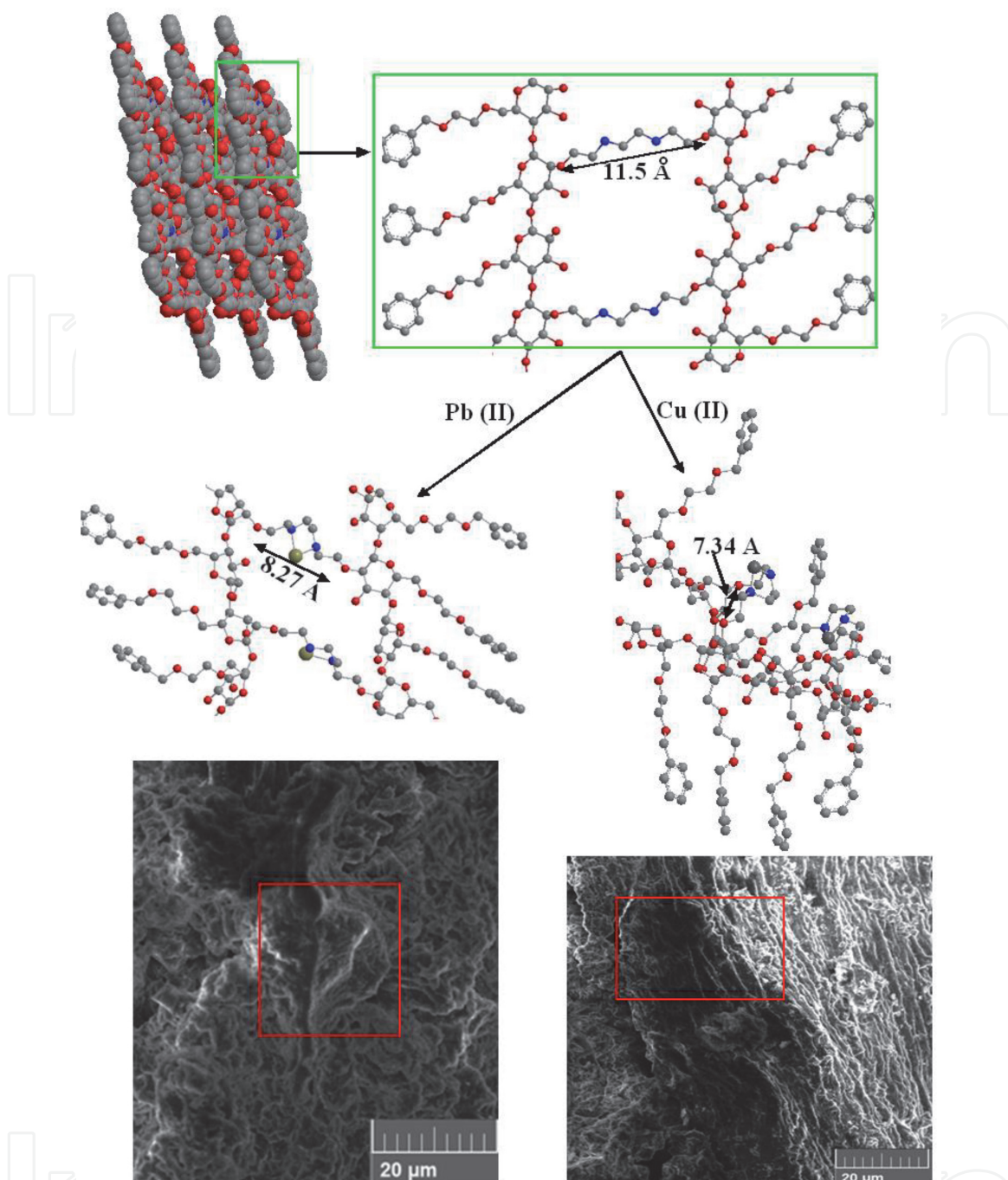
stronger interactions with the lone pairs of electrons of the nitrogen atoms of amino groups than that of the Cu, as previously demonstrated elsewhere [63, 85]. Therefore, the Pb(II) ions can rapidly form a stable complex with -NH<sub>2</sub> groups on the surface of the BEC- ED.

The adsorption isotherm was modeled both by Freundlich (Eq. (6)) and Langmuir (Eq. (7)) models. The results revealed that the equilibrium isotherms data (**Figure 12** and **Table 7**) correlated better with the Langmuir model with a maximum adsorption capacity estimated at 50.76 mg/g and 39.68 mg/g for Pb(II) and Cu (II), respectively. This implies that the BEC-ED surface is homogeneous, which indicates that lead and copper ions adsorption follows monolayer adsorption.

To better understand the retention mechanisms of copper and lead adsorption on BEC-ED, the effect of lead and copper ions adsorption on the morphology of BEC-ED was monitored by SEM analysis. **Figure 13** shows the possible interactions between BEC-ED and the Pb(II) and Cu (II) ions, as well as the proposed mechanism. SEM pictures showed distortion in the morphology of BEC-ED under the adsorption forces of Pb(II) and Cu(II) ions. However, this effect is probably caused by the interactions between the metal ions and the donor sites of the grafted groups (ED), where the internal compression of the laminated structure has caused a very remarkable separation of the polymeric layers. Indeed, the approximate calculation

	Langmuir				Freundlich		
	$q_{exp}$ (mg/g)	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	1/n	$K_F$ (L/mg)	$R^2$
Pb	43.85	50.76	0.137	0.996	0.443	6.1	0.951
Cu	36.64	39.68	0.112	0.990	0.5636	6.7	0.944

**Table 7.** Freundlich and Langmuir constants for lead and copper adsorption on BEC-ED.



**Figure 13.**  
*Impact of the adsorption of lead and copper ions on the morphology of BEC-ED.*

carried out to compare the inter-chain distances showed a decrease in the latter. The results obtained showed the capability of BEC-ED for adsorbing Cu(II) via metal interactions with  $\text{NH}_2$  groups of ethylenediamine [56, 60], resulting in the decrease in the inter-layer distance from 11.50 Å to 07.34 Å for copper and 08.27 Å for lead.

For the purpose to assess the potential retention of lead and copper ions retention provided by BEC-ED compared to other adsorbents, the results achieved through this study were compared with the adsorption abilities of some conventional natural and synthetic cellulose in the literature (**Table 8**). It has been found that the lead and copper retention capacity of BEC-ED is among the higher results. Therefore, considering the retention capabilities of other adsorbents, accessibility, environment friendly biomaterial, and low cost, it may be concluded that the BEC-ED adsorbent demonstrated its ability to efficiently eliminate lead and copper ions in simple media.

Grafted cellulose adsorbent	Chelating group	Metal ions	Adsorption capacity (mg/g)	Ref.
Cellulose	Epichlorohydrin	Pb <sup>2+</sup>	38.02	[86]
		Cu <sup>2+</sup>	72.99	
Microcrystalline cellulose	Tetrafluoroterephthalonitrile	Pb <sup>2+</sup>	20.46	[87]
		Cu <sup>2+</sup>	17.94	
Cellulosic biopolymer	(alkali treatment)	Pb <sup>2+</sup> ,	67.24	[88]
		Cd <sup>2+</sup>	44.42	
		Zn <sup>2+</sup>	16.85	
CMC@ hydrogel	—	Cu <sup>2+</sup>	2.30	[89]
BEC-ED	Ethylenediamine	Pb <sup>2+</sup>	50.76	this work
		Cu <sup>2+</sup>	39.68	this work

**Table 8.**  
*Comparison of lead and copper adsorption capacity of BEC-ED with conventional natural and synthetic cellulose adsorbents.*

4. Conclusion

A new green adsorbent, Benzyloxyethyl cellulose crosslinked ED (BEC-ED) was successfully synthesized. The proposal structures were confirmed using vibrational spectroscopy, X-ray diffraction patterns, SEM images, x-ray EDS spectra, and TGA thermograms. The results showed that the ED crosslinking reaction of BEC engendered new structural significant modification at the crystalline and morphological levels. Ethylenediamine crosslinked BEC has been used for the removal of lead (Pb) and copper (Cu) from an aqueous system. The results revealed that the equilibrium isotherms data correlated better with the Langmuir model with a maximum adsorption capacity estimated at 50.76 mg/g and 39.68 mg/g for Pb (II) and Cu (II), respectively. In addition, the results demonstrated that the capability of BEC-ED for adsorbing Cu (II) and Pb (II) was governed by metal–ligand interactions with NH<sub>2</sub> chelator sites of ethylenediamine, resulting in the decrease in the civility diameter from 11.50 Å to 07.34 Å for copper and 08.27 Å for lead. However, these distortions proved the lamellar structure, and the separation of the sheets was observed on the SEM images of BEC-ED after adsorption.

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Conflict of interest

The authors declared that there is no conflict of interest.

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