Modification of Lignocellulosic Materials with a Mixture of m-DMDHEU/Choline Chloride to Remove CrO$_4^{2-}$, NO$_3^-$, and H$_2$AsO$_4^-$ in Aqueous Solution

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1. INTRODUCTION

Several innovative materials have already proved their significant removal efficiency toward heavy metals, anions, and dyes. For instance, nano-zero-valent iron particles (nZVI) were applied to treat uranium, nitrate in aqueous solution, or Cr(VI) in soil; nZVI can remove heavy metals by redox reactions, precipitation/dissolution reactions, and adsorption/desorption process. A mixed iron-coated olive stone particles were developed to remove Cr(VI) in a tannery wastewater, where an olive stone plays a role as support to zero-valent iron and magnetite nanoparticles. Graphene oxide was used as the support to magnetic iron oxide to form nanocomposite material, the material can separate effectively Cd(II) ions in aqueous solution. Beside that, TiO$_2$–SiO$_2$–mixed oxide nanoparticles were developed as a heterogeneous photocatalysis, the material showed significantly higher methylene blue removal efficiency in comparison with that of the commercial TiO$_2$ material.

On the other hand, agricultural by-products were studied more and more to replace commercial anionite resins and commercial cationite resins in the treatment of ground water and wastewater because lignocellulosic materials have the advantages of a low cost, renewability, and easy functionalization process through an esterification reaction, etherification reaction, or nucleophilic substitution reaction. In addition, modified lignocellulosic materials also have high ability of adsorption and ion exchange in the removal of heavy metal cations and anions in aqueous solution. Therefore, the modification work was appreciated because of environmentally friendly, reducing water treatment cost, taking advantage of the available natural resources but still reaching the desired effect.

Lignocellulosic materials containing three main components are cellulose, hemicellulose, and lignin. Cellulose is the most abundant natural polymer on earth, reactive sites as nucleophiles are hydroxyl –OH groups located at positions of C6 and C2, especially the hydroxyl group of C6 because of the twist structure of cellulose chain, hydrogen bond, and unfavorable rearrangement at positions of C2 and C3 when the...

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reaction occurs.\textsuperscript{11,12} Lignin is not an expectant component in the modification process because they prevent the denaturation agent from contacting and reacting with hydroxyl groups of the cellulose chain. Therefore, lignin should be removed partially before modification, in case the lignin content in initial raw lignocellulosic materials is high, such as sawdust (23.0–28.8 wt %) and coconut shell (36.5 wt %).\textsuperscript{13,14} Many research studies were carried out to change their properties and functions by using different denaturation agents. Some inorganic acid and organic acid such as phosphoric acid, sulfuric acid, tartaric acid, succinic acid, oxalic acid, or citric acid were applied with the aim of binding negatively charged functional groups into the materials by using the esterification reaction. Negatively charged functional groups such as −COOH, −SO₃H, and −PO(OH)₂ could adsorb and exchange heavy metal cations with high efficiency. For example, Marshall et al. (1999) connected citric acid to soybean hulls in parched conditions to create cationite lignocellulosic materials possessing the ability to adsorb and exchange Cu(II) ions in aqueous solution\textsuperscript{15} or Li et al. (2008)-modified orange peel by citric acid to remove some ions such as Cd(II), Zn(II), Co(II), and Ni(II) effectively.\textsuperscript{16} On the other hand, positively charged functional groups such as groups of tertiary amines and quaternary amines were connected to the materials through cross-link bridges by using an etherification reaction. Some cross-link bridges applied, popularly in the recent times, were urea, dialdehyde, and epoxy. For instance, Marshall et al. (2005) connected choline chloride (CC) to soybean hull, sugarcane bagasse, and corn stover by using 4,5-dihydroxy-1,3-bis(hydroxymethyl)-imidazolidin-2-one (DMDHEU) in acidic and parched conditions to create anionic lignocellulosic materials possessing strong ability to absorb and exchange anions such as chromate, arsenate, and selenate in aqueous solution;\textsuperscript{17,18} Baipai and Rohit (2009) connected tertiary amine to sawdust by using epichlorohydrin and then the material applied to separate effectively chromate ions;\textsuperscript{19} or Park et al. (2014) connected CC to cellulose successfully by using dialdehyde in acidic conditions.\textsuperscript{20} These heavy metal cations and anions are directly associated with neurotoxicity, genetic mutation, cancer, as well as many adverse effects on living environment and ecosystem.\textsuperscript{21,22}

To the best of our knowledge, up to now the usage of cross-link bridge m-DMDHEU to connect CC to hydroxyl −OH groups of the cellulose chain in the treatment of groundwater have been not reported before (Figure 1). According to our quantum computational results, self-polymerization level of m-DMDHEU molecules is lower than other urea cross-link molecules, therefore the performance of the cross-link reaction will be higher.\textsuperscript{23} In this study, the mixture of m-DMDHEU/CC was used to modify three kinds of lignocellulosic materials containing different lignin contents and then applied to remove CrO₄²⁻, NO₃⁻, and H₂AsO₄⁻ anions in aqueous solution.

2. RESULTS AND DISCUSSION

2.1. Effect of wt % Ratio between m-DMDHEU and CC. There are −N(CH₃)₃Cl positively charged functional groups which appeared on the cellulose chain after modification, these groups play the main role in the anion exchange ability of modified lignocellulosic materials.

![Figure 1. Modification reaction of m-DMDHEU with hydroxyl −OH groups on cellulose chains and illustration of ion exchange mechanism.](https://dx.doi.org/10.1021/acsomega.0c01984)

\[
2\text{R} - \text{N(CH₃)₃Cl} + \text{CrO}_4^{2-} \\
\rightarrow (\text{R} - \text{N(CH₃)₃})_2\text{CrO}_4 + 2\text{Cl}^{-}
\]

\[
\text{R} - \text{N(CH₃)₃Cl} + \text{K}^+ + \text{CrO}_4^{2-} \\
\rightarrow (\text{R} - \text{N(CH₃)₃})\text{KCrO}_4 + \text{Cl}^{-}
\]

Activation time and liquor ratio were chosen suitably for the modification process, respectively, as 1 h and 1:60 in our heretofore survey results.\textsuperscript{24,25} Cotton, sawdust, and coconut shell powder were processed according to the modification process above, m-DMDHEU concentration ranging from 5 to 15 wt % and CC concentration ranging from 2 to 10 wt %. After being rinsed with distilled water, the materials were dried at room conditions and then the materials were weighed to determine the mass increase level of materials, and ion exchange capacity of the materials was also examined using 200 mL of 200 mg/L chromate solution at pH = 7.6 and room temperature (28 ± 5 °C). The results are presented in Figure 2.

m-DMDHEU cross-link bridges react strongly to hydroxyl −OH groups on the cellulose chain, but it does not make enhancements on the ability of ion exchange, while CC reacts weakly because of negligible mass increase level. The mass

![Figure 2. Mass increase level and ion exchange capacity according to the wt % ratio between m-DMDHEU and CC at reaction conditions (140 °C, 1 h, liquor ratio 1:60).](https://dx.doi.org/10.1021/acsomega.0c01984)
increase level decreases and ion exchange capacity increases when m-DMDHEU concentration is unchanged, and CC concentration ranges from 2 to 10 wt %. It could be because CC molecules occupy more −CH2−OH groups at high CC concentrations and prevent m-DMDHEU molecules from contacting and reacting with these reactive sites. The mass increase level accretes strongly and ion exchange capacity increases negligibly when the CC concentration is unchanged, and m-DMDHEU concentration ranges from 5 to 15 wt %.

Therefore, 5 wt % m-DMDHEU/10 wt % CC was chosen for the modification process in acidic and parched conditions. The results also revealed the relationship between lignin content in the initial lignocellulosic materials and efficiency level of the modification process, the following order: cotton > sawdust > coconut shell powder.

2.2. SEM Images and Specific Surface Area by Using the BET Method with Nitrogen Gas. Scanning electron microscopy (SEM) images of cotton before and after modification have unchanged diameter of fibers and in the range from 10 to 15 μm (shown in Figure 3I,II). The specific surface area of initial cotton measured by using the Brunauer–Emmett–Teller (BET) method with nitrogen gas was 724.955 m²/g, while the value of modified cotton was 0.000 m²/g. The unusual result could be explained by two reasons: first m-DMDHEU bridge form a cross-link between cellulose chains which lead to the diameter of pores on the modified cotton surface being reduced, congested, and destructed strongly; second the usage of nitrogen gas with a cross-sectional area of 0.162 nm² was bigger than the cross-sectional area of pores lead to nitrogen gas met difficulty in adsorption.

The specific surface areas of sawdust and coconut shell powder were 0.176 and 0.000 m²/g, respectively. The results were similar to the result of modified cotton. Modified sawdust has the diameter of wood fiber cell in the range from 10 to 15 μm, particle size distribution in the range from 200 to 400 μm (shown in Figure 3III), and bulk density 0.2099 g/cm³. Modified coconut shell powder has a hollow tube in an ellipse shape with a diameter of about 20 μm, particle size distribution in the range from 50 to 200 μm (shown in Figure 3IV), and bulk density 0.4843 g/cm³.

2.3. FT-IR and Solid-State 13C CP-MAS NMR Spectra. Fourier transform infrared spectroscopy (FT-IR) spectra of modified lignocellulosic materials show an additional peak at wavenumber 1708 cm⁻¹, these results confirmed the presence of the C=O group in the N−CO−N urea group. On the other hand, solid-state 13C CP-MAS NMR spectra of cotton after modification also show the speciality peak of the C=O group in the N−CO−N urea group at 159 ppm (shown in Figure 4). These results revealed that a chemical linkage was formed between m-DMDHEU and hydroxyl groups of the cellulose chain or CC.

2.4. pH_{pzc} Values and Effect of pH on Ion Exchange Capacity. Ion exchange capacity of modified lignocellulosic materials with a chromate solution was the best in acidic
conditions and dropped significantly in base conditions.\textsuperscript{24−26} The results could be explained by two reasons: first, OH\textsuperscript{−} ions and dichromate (Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}) ions were present in adsorbate solutions at different conditions; second, characteristic of modified material surface changed about charge, this matter could be checked by using the pH\textsubscript{PZC} value. When pH < pH\textsubscript{PZC} materials’ surface was charged positive and when pH > pH\textsubscript{PZC} materials’ surface was charged negative. pH\textsubscript{PZC} values of modified sawdust and modified coconut shell powder determined by using the graph method above were 11.7 and 11.6, respectively (shown Figure 5). The results were completely suitable and confirmed the experimental results before.

### 2.5. Effect of the Initial Chromate Concentration.

Chromate removal efficiencies of modified sawdust in batch mode and room temperature (28 ± 5 °C) with an initial chromate concentration in the range from 50 to 200 mg/L are presented in Table 1.

| \(m^a\) | \(t^b\) | \(C_0\) | \(C_e\) | \(q_e\) | \(H^c\) |
|---|---|---|---|---|---|
| 1.1706 | 12.0 | 50 | 7.1 | 7.3 | 85.8 |
| 1.1088 | 100 | 51.4 | 8.8 | 48.6 |
| 1.1244 | 150 | 95.7 | 9.7 | 36.2 |
| 1.1385 | 200 | 132.5 | 11.9 | 33.7 |

\(^a\)Dry mass. \(^b\)Contact time. \(^c\)Efficiency. The unit of \(C_0\) and \(C_e\) are mg/L; the unit of \(m\), \(t\), \(H\) are gram, hour, % respectively.

Based on the figures listed in Table 1, a graph of relationship between \(C_e/q_e\) and \(C_e\) was established, as shown in Figure 6.

![Figure 6. \(C_e/q_e\) relation to \(C_e\) for modified sawdust.](image)

The ion exchange capacities of modified sawdust with respect to dry mass, using about 1 g and initial chromate concentration in the range from 50 to 200 mg/L, were described to be compatible with the linearized Langmuir isotherm model (\(R^2 = 0.9633\)), and maximum ion exchange capacity was determined at \(Q_o = 12.0\) mg/g.

Chromate removal efficiencies of modified coconut shell powder in batch mode and room temperature (28 ± 5 °C) with the initial chromate concentration in the range from 100 to 200 mg/L are presented in Table 2.

| \(m^a\) | \(t^b\) | \(C_0\) | \(C_e\) | \(q_e\) | \(H^c\) |
|---|---|---|---|---|---|
| 1.1209 | 12.0 | 50 | 8.3 | 7.4 | 83.4 |
| 1.1492 | 100 | 56.2 | 7.6 | 43.8 |
| 1.0923 | 150 | 98.6 | 9.4 | 34.3 |
| 1.1215 | 200 | 142.3 | 10.3 | 28.9 |

\(^a\)Dry mass. \(^b\)Contact time. \(^c\)Efficiency. The unit of \(C_0\) and \(C_e\) are mg/L; the unit of \(m\), \(t\), \(H\) are gram, hour, % respectively.

Similar to the case of modified cotton above, the ion exchange capacities of modified coconut shell powder with respect to dry mass, using about 1 g and initial chromate concentration in the range from 50 to 200 mg/L, were described to be compatible with the linearized Langmuir isotherm model (\(R^2 = 0.9777\)) and maximum ion exchange capacity was determined at \(Q_o = 10.7\) mg/g (shown in Figure 7). The results revealed that adsorption and ion exchange process of anionite lignocellulosic materials with chromate in survey conditions happened reversibly on a single layer.

### 2.6. Evaluation of the Ability to Separate Chromate, Nitrate, and Arsenate Ions in a Fixed Bed Column.

![Image](image)

![Image](image)
fixed bed column containing specific dry mass of materials could treat the maximum volume of the adsorbate solution, respectively, and the outlet water still meets the permissible clean water standards. The maximum volume could be determined through a breakthrough curve. This study will not present about the breakthrough curve, instead that a specific volume of the adsorbate solution belongs to effective activity area of fixed bed column will be chosen to survey for the three application cases.

First, 200 mL of 200 mg/L CrO$_4^{2-}$ solution at pH = 7.6 was gone over a fixed-bed column with a diameter of 45 mm at room temperature (28 ± 2 °C). The result showed very high chromate removal efficiency of modified cotton, Cr(VI) was not detected in the treated solution. The chromate removal performance of modified cotton was better than that of the strong base anion resin anionite GA-13 at pH = 7.6 (see in Table 3). It could be explained by two reasons: first, cellulose skeleton of modified cotton is easier to wet than the polystyrene skeleton of anionite; second, the amounts of −N(CH$_3$)$_3$Cl functional groups were more than those of anionite.

When comparing with other treating methods, the ion exchange method by using modified cotton in fixed bed column also has high potential. For instance, Baracat and Schmidt (2010) achieved a removal efficiency of 93% when using the ultrafiltration method with an initial chromate concentration of 50 mg/L; 35 or Ozaki et al. (2002) reached a removal efficiency of 99% when using the RO filtration method with the initial chromate concentration of 167 mg/L. 34 Furthermore, the rate of Cr(VI) reduction in soil by nZVI nanoparticles (at a ×25 stoichiometric excess) was equal to 91% in batch mode with an initial chromate concentration of 55.48 mg/kg; or Cr(VI) removal efficiency of a mixed-iron coated olive stone nanoparticles was equal to 64.3% in fixed bed column with an initial chromate concentration of 17.4 mg/L in a tannery wastewater.

Second, 200 mL of 60.0 mg/L nitrate solution at pH = 2.9 was gone over a fixed-bed column with a diameter of 23 mm at room temperature (28 ± 2 °C). Nitrate was not detected in the treated solution (see in Table 4). The result confirmed again the very high anion removal efficiency of modified cotton when comparing with other innovative materials. For instance, nitrate removal efficiency of nZVI nanoparticles was equal to 40% with the initial nitrate concentration of 100 mg/L; 35 or nitrate removal efficiency of Cu-nZVI nanoparticles was close to 80% after 90 min in batch mode with the initial nitrate concentration of 62 mg/L.2

The removal efficiency of Ca(II) and Mg(II) ions was not good, and pH value was also increased from 2.9 to 4.2. The results revealed that the removal mechanism of modified cotton mainly complied with the anion exchange mechanism.

Finally, 100 mL of 2500 μg/L As(V) solution at pH = 7.0 was gone over a fixed bed column with a diameter of 30 mm at room temperature (28 ± 2 °C), the sample solution was contaminated with an arsenic concentration 50 times higher than that permitted in Vietnam National Technical Regulations QCVN 02:2009/BYT for living water and equivalent with an arsenic concentration level in groundwater in some areas of Vietnam. The results showed that modified sawdust and modified coconut shell powder also were fairly good anion exchange materials, outlet water meets the permissible living water standards for arsenic concentration under 50 μg/L, the arsenic concentrations in the treated solution for modified sawdust and modified coconut shell powder were, respectively, 44 and 35 μg/L (see in Table 5). At the current time, the desired arsenic concentration level is under 10 μg/L applied for drinking water in both Vietnam and some other countries in the world (According to Vietnam National Technical Regulations QCVN 01:2009/BYT, US Environmental Protection Agency, International Agency for Research on Cancer and WHO).36

### Table 3. Chromate Removal Efficiency of Materials in Fixed-Bed Column

| materials                  | m$^a$ | v$^b$ | C$_o$ | C$_e$ | H$^c$ |
|----------------------------|-------|-------|-------|-------|-------|
| modified cotton            | 10.0  | 5.0   | 200   | nd    | 100   |
| anionite GA-13             | 5.8   | 97.1  |       |       |       |

$^a$Dry mass. $^b$Flow rate. $^c$Efficiency, nd: not detected. The unit of C$_o$ and C$_e$ are mg/L; the unit of m, v, H are gram, mL/min, % respectively.

### Table 4. Nitrate Removal Efficiency of Modified Cotton in Fixed Bed Column

| ions   | m$^a$ | v$^b$ | C$_o$ | C$_e$ | H$^c$ |
|--------|-------|-------|-------|-------|-------|
| Ca(II) | 6.0   | 5.0   | 35.9  | 30.1  | 16.2  |
| Mg(II) | 34.2  | 28.9  | 15.5  |       |       |
| nitrate| 60.0  | nd    | 100   |       |       |

$^a$Dry mass. $^b$Flow rate. $^c$Efficiency, nd: not detected. The unit of C$_o$ and C$_e$ are mg/L; the unit of m, v, H are gram, mL/min, % respectively.

### Table 5. As(V) Removal Efficiency of Materials in Fixed Bed Column

| materials                  | m$^a$ | v$^b$ | C$_o$ | C$_e$ | H$^c$ |
|----------------------------|-------|-------|-------|-------|-------|
| modified sawdust           | 5.0   | 5.0   | 2500  | 44    | 98.2  |
| modified coconut shell powder | 35    |       |       |       | 98.6  |

$^a$Dry mass. $^b$Flow rate. $^c$Efficiency. The unit of C$_o$ and C$_e$ are μg/L; the unit of m, v, H are gram, mL/min, % respectively.

### 3. CONCLUSIONS

The removal mechanism of lignocellulosic materials modified with a mixture of m-DMDHEU/CC mainly complied with an anion exchange mechanism. Less lignin content in initial lignocellulosic materials is higher efficiency of modification.
process. A good working pH range of modified lignocellulosic materials are from 2 to 12. Outlet water under specific experimental conditions could meet the permissible drinking water standards for chromate and nitrate cases, and meet the permissible living water standards for the arsenic case. The results proved that modified lignocellulosic materials were very effective and potential ion exchange materials to replace for commercial anionite resin in the removal of anions in aqueous solution by using a fixed bed column.

4. MATERIALS AND METHODS

4.1. Raw Materials and Chemicals. The experiments are carried out with some chemicals detailed as below: m-DMDHEU 30 wt % of BASF, Germany; CC 98 wt % of Himedia, India; strong anion exchange resin GA-13 of Doshion, India; KH2AsO4 of Sigma-aldrich, Germany; and Ca(NO3)2, Mg(NO3)2, and K2CrO4 of Xilong, China. The desired solutions were prepared by mixing the chemicals together with distilled water without any further treatment. Cotton used in medicine with cellulose content above 98.0 wt %, sawdust from acacia auriculiformis wood, and powder of coconut shell in the Southern areas of Vietnam were used as the initial raw lignocellulosic materials.

4.2. Modification Process. The coconut shell was removed of impurities and milled; the powder was then screened through a 200 mesh screen and got solely the powder part under the screen. It is not necessary to carry out the delignification step for the cotton used in medicine because the lignin content is little.

Powder of coconut shell and sawdust were delignified in 0.2 N NaOH solution with 70% v/v ethanol and 30% v/v water. The materials, after removing lignin partially, were immersed in 5 wt % m-DMDHEU and 10 wt % CC solutions in the range of set pH value (pH = 3 ± 4) for 24 h so that the solution could infiltrate deeply between the fibers; after 24 h, the materials were filtered out, dried at room temperature conditions until their moisture content was lower than 15 wt %; finally, the materials were activated at 140 °C for 1 h. The activated materials were then rinsed thoroughly with distilled water, dried, and stored in polyethylene bags. The mass increase level and ion exchange capacity are combined to evaluate and choose appropriate parameters for the modification process.

4.3. Measuring and Analysis Equipment. Mass of solid materials was measured on a SARTORIUS CPA224S analytical scale and moisture content was determined with a SARTORIUS MA35 moisture analyzer. The morphological characteristics of materials were observed by using HITACHI S4800 scanning electron microscope machine, specific surface areas of materials were measured by the BET method on an instrument Nova Station A using the nitrogen gas. The functional groups were characterized by FT-IR spectra with TENSOR 37 machine and by solid-state 13C CP-MAS NMR spectra with JNM-ECZ600R machine.

Chromate concentration was measured with a SHIMADZU AA-6300 atomic absorption spectrophotometer, nitrate concentration was determined by the ion exchange chromatography method and As(V) concentration was measured with an Agilent 7500 ICP-MS system. Ion exchange capacity q (mg/g) was calculated by using the following formula.

\[ q = \frac{(C_i - C_f)V}{m \cdot 1000} \]  

where \( C_i \) (mg/L) is the initial concentration of anion or atom in adsorbate solution; \( C_f \) (mg/L) is the equilibrium concentration of anion or atom in adsorbate solution; \( V \) (mL) is the volume of adsorbate solution; and \( m \) (g) is the dry mass of ion exchange materials (the rest of materials mass after the water content due to moisture have been removed).

Maximum ion exchange capacity \( q_e \) (mg/g) was determined by using the linearized Langmuir isotherm model.

\[ \frac{1}{q_e} = \frac{1}{b \cdot Q_o} + \frac{1}{Q_o} \]  

where \( q_e \) (mg/g) is the equilibrium ion exchange capacity with respect to the initial concentration \( C_o \); \( b \) (mg/L) is the coefficient related to the affinity between ion exchange materials and adsorbate; and \( Q_o \) (mg/g) is the maximum ion exchange capacity.

Modified lignocellulosic materials were determined the pH\textsubscript{PZC} value by using the measuring method as shown below: 6 conical flask 100 mL were prepared, 25 mL of 0.1 M NaCl solution were filled out into each of the flasks; and then pH of the solutions was adjusted before ion exchange (pH\textsubscript{f}) in the range of the variable value from 2 to 12 by using 0.1 M HCl solution or 0.1 M NaOH solution. After that, 0.25 g of ion exchange materials was added to each of the flasks, and magnet fishing was used to agitate evenly for 90 min; finally, filtration was carried out and the refined solutions were obtained to measure the pH values (pH\textsubscript{e}). The curve represents the relationship between \( \Delta pH = pH_f - pH_e \) and pH, intersecting with the horizontal axis at a point. pH value at the point is the pH\textsubscript{PZC} value.

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