Application of Sawdust modified with m-DMDHEU/ Choline chloride for the removal of \(\text{CrO}_4^{2-}\) and \(\text{H}_2\text{AsO}_4^{-}\) in water

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Abstract. This article studies the use of *acacia auriculiformis* wood sawdust modified with 4,5-dihydroxy-1,3-bis (methoxymethyl) imidazolidin-2-one (m-DMDHEU) and choline chloride for separating \(\text{CrO}_4^{2-}\) and \(\text{H}_2\text{AsO}_4^{-}\) ions in water. NaOH 0.2N/ ethanol 70° solution was used to remove lignin from the raw material, the material was then immersed in m-DMDHEU/choline chloride aqueous solution for 24 hours, after that the material was activated at 140°C for one hour. The ability to adsorb and exchange ions of the material was examined using solutions containing \(\text{CrO}_4^{2-}\) and \(\text{H}_2\text{AsO}_4^{-}\) ions in different conditions. The results suggested that the ability to separate \(\text{CrO}_4^{2-}\) and \(\text{H}_2\text{AsO}_4^{-}\) ions of the modified material was better than that of anion resin at pH = 7.0; the chromate adsorption capacity was the highest in acidic condition; the presence of arsenate (V) anions had no effect on the ability to remove chromate. Lastly, the modified material was used to treat water samples containing concentrations of arsenic similar to groundwater in several arsenic-contaminated areas of Vietnam.

1. Introduction

From mining activities, tanneries, electronics industries, metal plating, lead-acid battery manufacture, petroleum refining, or textile and dyeing industries, etc. a large amount of heavy metals like Fe, Cu, Pb, Ni, Cd, As, Hg, etc. has been discharged [1,4]. These heavy metal are directly associated with genetic mutation, cancer, as well as many adverse effects on the environment [1,2]. For developing countries like Vietnam, the industrial activities are usually conducted on a small scale or medium scale, thus wastewater treatment can be a difficult task because of the high cost. For that reason, agricultural by-products are being studied for water treatment due to their benefits: low cost, renewability, and they are mostly made of polymers which are easy to modify and have a high potency for adsorption/ion exchange [1-3,5].

Citric acid is commonly used as the modifying agent for cellulose to remove metals in cation form such as Fe, Cu, Pb, and Ni, etc. Compared with previous methods to modify cellulose, citric acid shows many advantages: low cost, simple condition for reaction, citric acid is non-toxic, modified material gives a high performance in ion separation [6-11].

To separate metals in anions such as chromate, arsenate, etc. have just had a few published researches on using modified cellulose [12-14]. Notably, Marshall et al. (2005) carried out experiments to modify soybean hulls, sugarcane bagasse, and corn stalks using DMDHEU and choline chloride (CC) as modifying agents. The separation of chromate, arsenate, and selenate ions was significantly enhanced [12].

In this research, sawdust was modified with 4,5-dihydroxy-1,3-bis(methoxymethyl)imidazolidin-2-one (m-DMDHEU) and choline chloride following the mechanism illustrated in Figure 1 [14].
After modification, there are –N(CH₃)₃Cl groups on the cellulose chain, these groups play the main role in the ability to exchange ions of the modified material.

\[
2R·3(CH₂)₃Cl + CrO₄^{2-} \rightarrow (R·N(CH₃)₃)₂CrO₄ + 2Cl^- \\
R·3(CH₂)₃Cl + K^+ + CrO₄^{2-} \rightarrow (R·N(CH₃)₃)₂KCrO₄ + Cl^- 
\]

2. Materials and methods

2.1 Materials

The chemicals used in the experiments are: m-DMDHEU 30% produced by BASF; choline chloride 98% made in India; K₂CrO₄; KH₂AsO₄; anion resin GA13 made in India; and distilled water. The desired solutions were prepared by mixing the chemicals with distilled water without any further treatment. Sawdust from acacia auriculiformis wood was used as the base material.

2.2 Process of sawdust modification

Sawdust was immersed in m-DMDHEU 5% and choline chloride 10% solution at a set pH (pH = 3–4) for 24 hours so that the solution could infiltrate deep between the fibers; after 24 hours the material was filtered out, dried at room condition until its moisture content was lower than 20%; after that the material was activated at 140°C for 1 hour. The activated material was then rinsed thoroughly with distilled water, dried at room condition and stored in plastic bags.

2.3 Equipment

Measuring of the solid materials was done on SARTORIUS CPA2245 analytical scale and moisture content was determined with SARTORIUS MA35 moisture analyzer at the Laboratory of Organic Chemical Engineering, University of Technology, HCMC; chromate concentration was measured with SHIMADZU AA-6300 atomic absorption spectrophotometer and arsenate concentration was measured with Agilent 7500 ICP-MS system at the Laboratory of Analytical Chemistry, University of
Science, HCMC; FT-IR spectra of the material before and after modification were obtained at the Key Laboratory of Chemical Engineering and Petroleum Processing, University of Technology, HCMC.

3. Results and discussion

3.1 Effect of activation time

The sawdust was processed with procedure similar to that in section 2.2, the effect of activation time (ranging from 0.5 hours to 3 hours) was evaluated. After being rinsed with distilled water, the material was dried at room condition, then the material was weighed to determine the increase in the mass of material, the capacity of the material to exchange ions was also examined using 200 ml of solution containing chromate 200 ppm at pH = 7.6 and room temperature (28±5°C). The results are presented in Table 1.

| Time (hour) | Dry matter (g) | Dry matter after activation (g) | Mass increase (g/g) | mmol CrO$_4^{2-}$/g of dry matter |
|------------|----------------|-------------------------------|---------------------|---------------------------------|
| 0          | 0.9476         | 0.9666                        | 0.02                | 0.012                           |
| 0.5        | 0.9517         | 1.0278                        | 0.08                | 0.071                           |
| 1          | 0.9118         | 1.0851                        | 0.19                | 0.101                           |
| 1.5        | 0.9143         | 1.0423                        | 0.14                | 0.074                           |
| 2          | 0.9412         | 1.0542                        | 0.12                | 0.065                           |
| 3          | 0.9216         | 1.0322                        | 0.12                | 0.054                           |

There was a significant increase in mass and capacity after activation. At activation time of 0 hour the increase of mass was unnoticeable and the ion-exchange capacity was little. It can be explained as there was no reaction between m-DMDHEU/CC and sawdust at 0 hour, the chromate ions were merely adsorbed on to the surface of the material.

Maximum increase of mass (0.19 g/g) and maximum capacity (0.101 mmol/g) was achieved at 1 hour. A conclusion can be made that after 1 hour, there was no more reaction between CC and sawdust through m-DMDHEU linkage. By combining the results, the chosen optimum for activation time was 1 hour.

3.2 Effect of liquor ratio

The sawdust was processed with procedure similar to that in section 2.2, with liquor ratio ranging from 1:20 to 1:100. The results are presented in Table 2.

| Liquor ratio | Dry matter (g) | Dry matter after activation (g) | Mass increase (g/g) | mmol CrO$_4^{2-}$/g of dry matter |
|--------------|----------------|-------------------------------|---------------------|---------------------------------|
| 1:20         | 1.1612         | 1.3360                        | 0.15                | 0.081                           |
| 1:60         | 1.1684         | 1.3904                        | 0.19                | 0.103                           |
| 1:100        | 1.0896         | 1.2857                        | 0.18                | 0.101                           |

The mass increase and ion-exchange capacity of the material rose when the liquor ratio was raised from 1:20 to 1:60, and remained approximately the same when liquor ratio was raised from 1:60 to 1:100. This can be explained as when the liquor ratio is low, the diffusion of the substances into the fibers is hindered, resulting in a low impregnation efficiency.
3.3 FT-IR spectra of sawdust

![FT-IR spectra of sawdust](image)

**Figure 2.** FT-IR spectra of sawdust before (a) and after (b) modification.

Compared to the spectrum of sawdust before modification, there is an additional peak at wavenumber 1708 cm\(^{-1}\) in the spectrum of modified sawdust, this indicates the presence of C=O group in the N-CO-N urea group. This indicates that there was reaction between m-DMDHEU, choline chloride, and sawdust.

3.4 Effect of pH on ion-exchange capacity

Three tests were carried out using a solution containing chromate 200 ppm, 200 ml of solution was used for each test, and each test was conducted at a different pH value. The results are presented in Table 3.

| pH   | Condition | Dry matter (g) | mmol CrO\(_4^{2-}\)/g of dry matter |
|------|-----------|----------------|-------------------------------------|
| 3.2  | Acidic    | 1.07           | 0.161                               |
| 6.8  | Neutral   | 1.05           | 0.103                               |
| 10.3 | Basic     | 1.05           | 0.078                               |

The results showed that in acidic condition, the ion-exchange capacity was the best. In basic condition, the capacity of the material dropped significantly, the reason is the presence of OH- ions, they occupied the ion exchanging sites and prevented contact with chromate ions, leading to a drop in ion-exchange capacity of the material. Meanwhile in acidic condition, chromate ions form dichromate ions (Cr\(_2O_7^{2-}\)), which have the same electrical charge as chromate ions (CrO\(_4^{2-}\)), but greater molecular mass, and double the amount of chromium atoms; in other words, with the same number of ion exchanging sites, the material can separate more chromate ions from water in acidic condition.

3.5 Evaluation of the ability to separate chromate and arsenate ions in a packed column

The solution containing CrO\(_4^{2-}\) and H\(_2\)AsO\(_4^-\) ions at pH = 7.0 was used to assess and compare the efficiency of the modified sawdust with high-quality commercial anion resin. The columned used in the experiment had a diameter of 30 mm; the experiment was carried out at room temperature (28 ± 2 °C). The results are presented in Table 4.
Table 4. Efficiency of ion separation process in packed column

| Target anion                  | CrO$_4^{2-}$ | H$_2$AsO$_4^-$ |
|-------------------------------|--------------|---------------|
| Modified sawdust (g), (dry matter) | 10           |               |
| Flow rate (ml/min)            | 5            |               |
| Total volume (ml)             | 200          |               |
| Concentration (ppm)           | 100          | 50            |

| After using sawdust           | Concentration (ppm) | 0.87 | 0.04 |
|                              | Efficiency (%)      | 99.1 | 99.9 |
| After using anion resin       | Concentration (ppm) | 2.0  | 1.2  |
|                              | Efficiency (%)      | 98.0 | 97.6 |

As shown in the results, the presence of arsenate ions did not interfere with the ability of the material to separate chromate ions. The efficiency of the ion exchanging process was almost ideal, yielding 99.1 % for chromate ions and 99.9 % for arsenate ions, meanwhile the values obtained with anion resin were 98.0 % and 97.6 %, respectively.

3.6 Treating water containing arsenic in a packed column

The modified sawdust was used to treat water with a high arsenic concentration similar to groundwater from tube wells in arsenic-contaminated areas in Vietnam. The arsenic concentration of the prepared water sample was 2500 ppb, which is 50 times higher than permitted in Vietnam National Technical Regulation QCVN 02:2009/BYT. The columned used in the experiment had a diameter of 30 mm; the experiment was carried out at room temperature (28 ± 2 °C); the flow rate was 5 ml/min; pH of the water sample was at 7. The results are presented in Table 5.

As seen in Table 5, the efficiency of the treatment was 98.2%. Furthermore, the concentration of arsenic after treatment was 44 ppb; this is below the permitted concentration.

Table 5. Efficiency of water treatment

| Target element                  | As |
|---------------------------------|----|
| Modified sawdust (g), (Dry matter) | 5  |
| Flow rate (ml/min)              | 5  |
| Total volume (ml) | 100 |
|------------------|-----|
| Concentration (ppb) | 2500 |
| Concentration after treatment (ppb) | 44 |
| Efficiency (%) | 98,2 |
| Permitted concentration (ppb) | 50 |

4. Conclusion

From the results of this study, it can be concluded that there was a significant increase in the ability of sawdust to adsorb and exchange chromate ions after being modified with m-DMDHEU and choline chloride. Compared with commercial anion resin, the performance in separating chromate and arsenate ions of modified sawdust was better at pH=7.0. Modified sawdust can be applied for treating contaminated groundwater with arsenic concentration 50 times higher than permitted in Vietnam National Technical Regulations. In conclusion, m-DMDHEU was proven to be an effective agent to link choline chloride to cellulose chain; this suggested a new approach to produce lignocellulosic anion exchangers from other agricultural by-products to separate heavy metal anions in aqueous solution [14].

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