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Synthesis of cellulose graft ionic liquid using silanization reaction

Thi Lan Nhi Do¹, Ngoc Lan Anh Do¹, Minh Huy Do², Ut Dong Thach^{1,*}

ABSTRACT

Introduction: Ionic liquids (ILs) have attracted many attentions due to their interesting physico-chemical properties. However, ionic liquids have several disadvantages including high viscosity, difficult to purify, separate and recycle, and expensive. Therefore, supported ionic liquids (SIL) have been developed to overcome these problems. SIL based on cellulose material was conventionally synthesized by silanization reaction between ionic liquid trialkoxyl silane and hydroxyl groups on the surface of cellulose. However, low reactivity of cellulose hydroxyl groups causes the low efficiency of silanization reaction. With the aim to resolve these problems and improve the reactivity of cellulose silanization reaction, cellulose graft ionic liquid was synthesized and characterized.

Methods: Cellulose graft ionic liquid (CL-IL) material was synthesized by silanization reaction. The influence of reaction condition such as IL/CL (w/w) ratio, base catalyst (NH₃) and agent coupling tetraethyl orthosilicate (TEOS) on silanization reaction was investigated. The modified CL-IL materials were characterized using FT-IR, TGA, SEM. The ion exchange properties were evaluated via batch adsorption studies to evidence the efficiency of silanization reaction of cellulose. **Results:** The study indicated that adding TEOS with NH₃ catalyst could significantly increase the number of imidazolium groups grafted on cellulose about 75% compared to the conventional approach. CL-IL material is an efficient anion exchange materials displaying fast kinetic adsorption and high capacity adsorption of MO up to 1.4 mmol g⁻¹. **Conclusion:** High-efficiency of cellulose silanization was obtained by using coupling agent TEOS and base catalyst. Therefore, the silanization reaction can be used for synthesis divers of functional cellulose materials. This approach can be aimed for the design of cheaper and high-performance materials for catalysis, polymer composite and adsorption in water treatment and depollution of industrial wastewater.

Key words: cellulose, ionic liquid, adsorption, ion exchange

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INTRODUCTION

In recent years, ionic liquids (ILs) have attracted many attentions due to their interesting physicochemical properties such as low vapor pressure, thermally and chemically stable, low combustibility, and favorable interaction properties with a range of organic and inorganic compounds.¹ However, ionic liquids have several disadvantages including high viscosity, difficult to purify, separate and recycle, and expensive for the use as a solvent in organic synthesis and liquid/liquid extraction.² Supported ionic liquids (SIL) have been developed to overcome these problems.^{3,4} SILs are hybrid material combined the benefits of the ionic liquid characteristic with the recyclability and hydrothermal stability of support. These materials have high potential application in catalysis and separation.⁵⁻¹⁰

Cellulose is the most abundant polymer on Earth. This biopolymer has been studied for applications in many areas such as catalysis,² adsorption¹¹⁻¹⁵ and polymer composites.¹⁶ These applications are based on surface modification of hydroxyl group on the sur-

face of cellulose, for example, esterification, etherification, tosylation, and silanization. Silanes are recognized as an efficient coupling agent for mineral oxides such as SiO₂, TiO₂, and Al₂O₃. The silane coupling agents have also been of interest in applying for cellulose, since both mineral oxide and cellulose bear hydroxyl group on their surface. Several studies for surface functionalization of cellulose by silanization reaction have been reported.^{2,17} However, insufficient reactivity silanization is observed due to the low reactivity of hydroxyl groups of cellulose.¹⁷ Thus, the high-efficiency of cellulose silanization is desirable.

We herein report the synthesis of cellulose graft ionic liquid, a novel SIL material, using silanization reaction. The aim of this study is to improve the efficiency of cellulose silanization. It is well known that tetraethyl orthosilicate (TEOS) is higher reactive than trialkoxyl silane coupling agent. Therefore, the influences of synthesis condition such as the IL/CL (w/w) ratio, the reaction medium (neuter or basic) and the presence of tetraethyl orthosilicate (TEOS) were investigated. The modified cellulose materials

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were characterized by FT-IR, SEM, and TGA. Furthermore, ion exchange properties of methyl orange (MO) onto modified cellulose were evaluated to evidence the efficiency of silanization reaction of cellulose.

METHODS

Chemicals

Cellulose fiber (medium), (3-chloropropyl) trimethoxysilane (97%), 1-methylimidazole (99%), methyl orange (85%), and tetraethyl orthosilicate (98%) from Sigma-Aldrich were used without further purification.

Preparation of ionic liquid

The IL (1-(trimethoxysilylpropyl)-3-methylimidazolium chloride) was synthesized following to previously described protocol². In a representative procedure, (3-chloropropyl) trimethoxysilane (10 mmol) and 1-methylimidazole (10 mmol) were added in a well-dried 250 mL three-neck flask. The flask was evacuated and purged with nitrogen three times. Then, the mixture was stirred at 90 °C for 48 h under nitrogen atmosphere. The reaction system was then cooled at room temperature. The unreacted reactants were eliminated by thorough washing with 15 mL dry ethyl acetate four times. Finally, the ionic liquid product was dried under vacuum for 24 h at room temperature. ¹H NMR (500 MHz, DMSO, δ , ppm) : 0.54 (m, 2H), 1.80 (m, 2H), 3.16 (s, 9H), 3.91 (s, 3H), 4.23 (m, 2H), 7.76-8.08 (m, 2H), 9.75 (s, 1H).

Preparation of CL-IL

The CL-IL materials were prepared using a previously described procedure with a slight modification.² In a representative protocol, the ionic liquid was dissolved in a mixture of ethanol: water (80: 20 v/v) at a concentration of 10% (w/w) and stirred at room temperature for 12 h. Then, suspension of 1 g cellulose fiber, 5 mmol of NH₃ and 5 mmol of TEOS were prepared in 10 mL of the mixture of ethanol: water (80: 20 v/v). The IL solution was added in cellulose suspension and the mixture was stirred at room temperature for 8 h. Afterward, the solvent was eliminated by an evaporator. The obtained white solid was thermally treated at 110 °C for 3 h. The final material was washed thoroughly with 50 mL ethanol three times and dried at room temperature to eliminate unreacted products. Various modified CL-IL materials were prepared in different conditions (*e.i.* with or without catalyst and TEOS). The detailed name and composition of materials were shown in **Table 1**.

Characterization

¹H NMR spectroscopy was accomplished using 500 MHz Burker Avance DRX NMR Spectrometer. FT-IR spectroscopy was carried out using an FT-IR Jasco 6600. TGA analysis was performed on TGA Q500 instrument. All materials were analyzed under oxygen atmosphere between 25 and 900 °C at a heating rate of 5 °C/min. Scanning electron microscopy (SEM) images were conducted using a JEM-1400, 100 kV.

Batch Adsorption Studies

The adsorption isotherms of methyl orange (MO) onto CL-IL were established by shaking about 10 mg of modified cellulose with 20 mL of MO solution in a 50 mL centrifuge tubes. The initial concentrations of MO were varied in the range: 0.10-2.00 mmol L⁻¹. The pH of MO initial solution is 6.7. The mixtures were slowly shaken at 25 °C for 2 h. The kinetic adsorption was studied at pH 6.7, by shaking about 10 mg of modified cellulose and 20 mL of MO solution (1.00 mmol L⁻¹) for different intervals of time in the range 2-200 min. After this time, the MO solution of the supernatant was filtered and determined by UV spectroscopy V-670 Jasco ($\lambda = 464$ nm). The quantity adsorbed (Q_{ads} , mmol g⁻¹) were determined by the following formula :

$$Q_{ads} = \frac{(C_i - C_e) V_0}{m_s} \quad (1)$$

where C_i (mmol L⁻¹) and C_e (mmol L⁻¹) are the initial and equilibrium concentration of MO solution. V_0 (L) is the total volume of the aqueous solution and m_s (g) is the mass of solid. All adsorption experiments were carried out in duplicate.

RESULTS

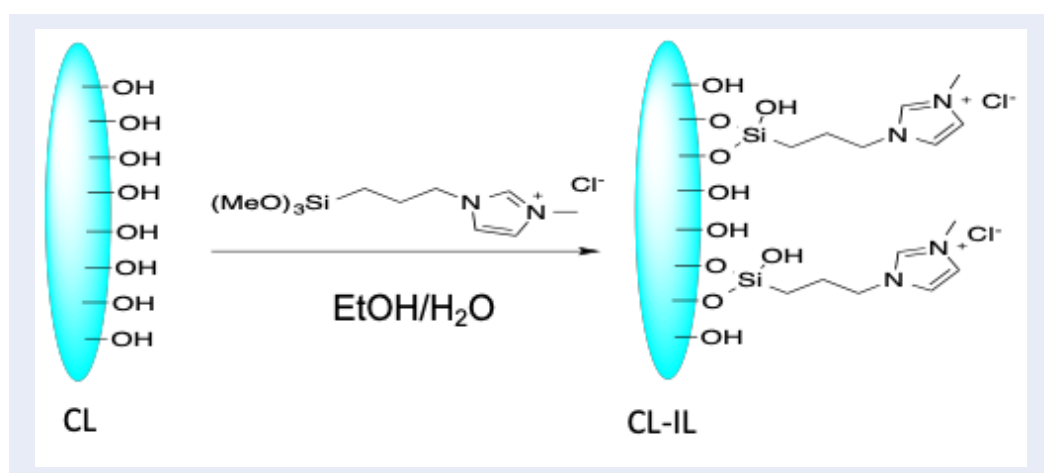
Synthesis of CL-IL

The modified CL-IL was synthesized by the silylation modification of cellulose (**Scheme 1**). The formation of CL-IL materials was confirmed using FT-IR, TGA, and SEM.

The FT-IR spectra of cellulose, ionic liquid, and modified CL-IL material were shown in **Figure 1**. For the CL-IL-0.5 material, the presence of imidazolium groups on cellulose surface was confirmed by the weak adsorption band at about 1569 cm⁻¹, corresponds for double bond C=N of imidazolium ring. For CL-IL-TEOS material, the FT-IR spectrum demonstrates a medium absorption band at 1569 cm⁻¹. Additionally, we observed two new weak absorption bands at 3085 and 3153 cm⁻¹, characterize

Table 1: Detailed of name and compositions for the preparation of modified CL-IL materials

Materials	IL (g)	NH ₃ (mmol)	TEOS (mmol)
CL-IL-0.1	0.1	-	-
CL-IL-0.3	0.3	-	-
CL-IL-0.5	0.5	-	-
CL-IL-NH ₃	0.5	5	-
CL-IL-TEOS	0.5	-	5
CL-IL-TEOS-NH ₃	0.5	5	5



Scheme 1: Reaction silanization of cellulose with ionic liquid.

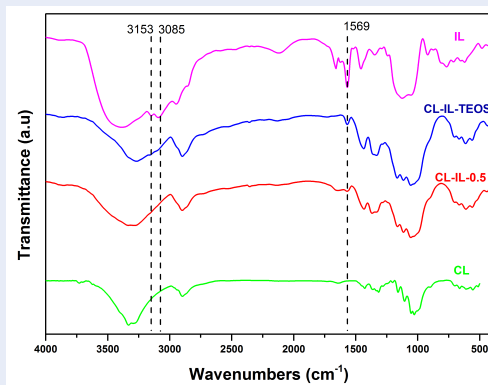


Figure 1: Comparison of FT-IR spectrum of, materials, CL: cellulose (green line); CL-IL0.5: modified cellulose with ration IL/CL(w/w) 0.5/1 (red line); modified cellulose with TEOS (blue line) and ionic liquid (pink line).

for the stretching vibration of unsaturated C-H bond of imidazolium ring.²

Thermal stability and composition of CL and CL-IL materials were carried out using thermogravimetric analysis (TGA). TGA plot of CL, CL-IL-0.5, and CL-IL-TEOS-NH₃ are shown in Figure 2. TGA analyses demonstrate CL and modified CL have similar thermal stability and start to decompose at about 300 °C. The residual weight percent for CL, CL-IL-0.5, and CL-IL-TEOS are 1, 4 and 15%, respectively. The residual weights for modified CL are related to the formation of SiO₂ during the TGA analysis condition under the oxygen atmosphere.

Scanning electron microscopy (SEM) was then used to characterize the morphology of materials. The SEM images of CL-IL-0.5 and CL-IL-TEOS-NH₃ are shown in Figure 3. The SEM images of ionic liquid modified cellulose without TEOS (CL-IL-0.5) showed the fiber structure of cellulose with the diameter of fiber about 20 μm and a relatively homogeneous surface of the fiber. In the SEM image of modified cellulose with TEOS, we observed the formation of equant particles with the diameter about 1-6 μm on the surface of modified cellulose fiber. These particles can be referred to the formation of SiO₂ particles on the surface of cellulose during the functionalized conditions.

Adsorption properties

Kinetic study. Adsorption kinetic of ion exchange material is an important parameter for the potential application in wastewater treatment. Therefore, the adsorption kinetic MO onto CL-IL was studied. The effect of contact time on quantity adsorbed of MO onto the representative material CL-IL-TEOS-NH₃ was shown in Figure 4. The results demonstrated that kinetic adsorption of ion exchange is fast. About 90 % of MO exchange is reached after 10 min and the saturation of ion exchange is reached after 120 min. The detailed kinetic parameters were determined using Lagergren pseudo-first-order model¹⁸ and pseudo-second-order model^{19,20}. The non-linear method was used to calculate the best-fit kinetic model. The calculated result of kinetic parameters is shown in Table 2. The pseudo-second-order model is suitable to describe the kinetic adsorption of MO onto modified CL-IL material. This result suggests that the sorption process occurs via electrostatic interaction mechanism.^{21,22}

Adsorption Isotherm of MO. The influence of IL/CL(w/w) ratio on the adsorption of MO onto CL-IL materials was studied. The adsorption isotherms of MO on CL, CL-IL-0.1; CL-IL-0.3 and CL-IL-0.5

are shown in Figure 5a. MO adsorption capacity of CL is very low. While the adsorption capacity of MO onto modified CL-IL is 0.2, 0.4 and 0.8 mmol g⁻¹ for CL-IL-0.1, CL-IL-0.3, and CL-IL-0.5, respectively. That means the adsorption capacity of MO increase with increasing of IL/CL(w/w) ratio. The increasing of MO adsorption capacity is due to the number of imidazolium groups grafted on the surface of CL material.

We then studied the influence of the catalysis NH₃ on adsorption of MO. The material CL-IL-NH₃ was synthesized in the same condition with CL-IL-0.5 with the presence of NH₃. Sorption isotherms of MO on CL-IL-0.5 and CL-IL-NH₃ were shown in Figure 5b. The results demonstrated that two modified cellulose materials showed similar adsorption isotherm.

The influence of TEOS on MO adsorption capacity was finally studied. The modified CL-IL materials synthesized with or without TEOS were used for this study. Figure 5c shows the sorption isotherms of MO on CL-IL-0.5; CL-IL-TEOS and CL-IL-TEOS-NH₃. We observed that the CL-IL synthesized in the presence of agent coupling TEOS have a higher adsorption capacity than CL-IL synthesized without TEOS. Interestingly, CL-IL material synthesized in the presence of TEOS and NH₃ shows the best adsorption properties with quantity adsorbed up to 1.4 mmol g⁻¹. That means the formation of CL-IL materials is favorable with the presence of agent coupling TEOS and base NH₃.

DISCUSSION

The synthesis condition such as ratio ionic liquid/cellulose (w/w), catalyst (NH₃), and adding TEOS defined considerable influence on the cellulose silanization reaction. The number of ionic groups graft on cellulose increased with increasing the ratio ionic liquid/cellulose (w/w). The maximum number of imidazolium groups grafted is 0.8 mmol per gram cellulose with the ratio ionic liquid/cellulose (w/w) of 0.5/1. However, the base catalysis (NH₃) has no influence on the silanization reaction. Interestingly, the addition of TEOS defined a considerable impact on the silanization reaction. Adding only TEOS in the reaction improved about 25% of number imidazolium groups grafted on cellulose (1.0 mmol⁻¹). Additionally, the silanization reaction was carried out with TEOS and base catalysis NH₃ improved about 75% of number imidazolium group grafted on cellulose (1.4 mmol⁻¹). Adding TEOS and base catalysis favored the formation of SiO₂ particle on the surface of cellulose, and therefore, improve the silanization coupling between cellulose and silane coupling agent.

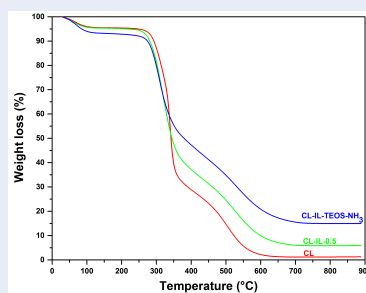


Figure 2: TGA plots of materials, CL-cellulose (red line); CL-IL-0.5: modified cellulose with ration IL/CL(w/w) 0.5/1 (green line) and CL-IL-TEOS-NH₃: modified cellulose with TEOS and NH₃ (blue line)

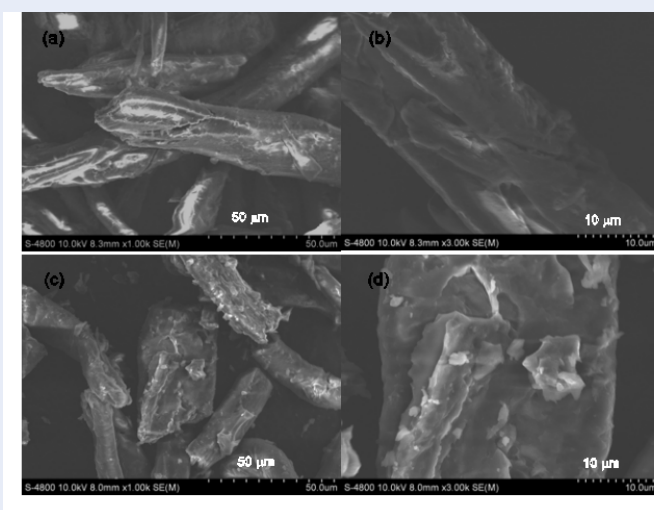


Figure 3: SEM images of materials at different magnification, (a), (b) : CL-IL-0.5, modified cellulose with ration IL/CL(w/w) 0.5/1 and (c), (d) : CL-IL-TEOS-NH₃, modified cellulose with TEOS and NH₃

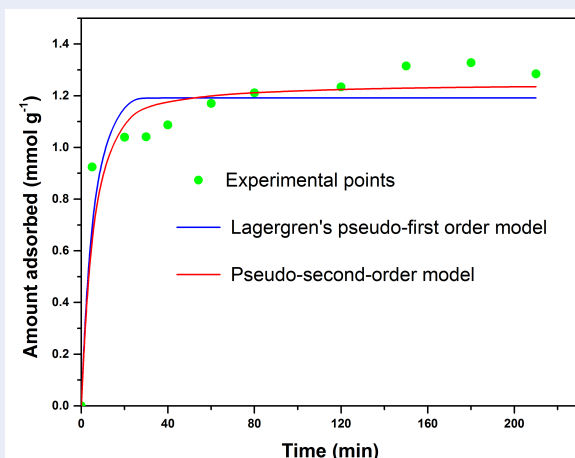


Figure 4: Effect of contact time on adsorption of MO onto CL-IL-TEOS-NH₃ materials (green points), the fitted data from the Lagergren pseudo-first order (blue line) and pseudo-second-order model (red line) calculated using the non-linear method

Table 2: Adsorption kinetic properties of MO onto CL-IL-TEOS-NH₃

Material	Lagergren pseudo-first-order model			Pseudo-second-order model		
	$Q_{e.cal.}$ (mmol g ⁻¹)	K_1 (min ⁻¹)	R_1^2	$Q_{e.cal.}$ (mmol g ⁻¹)	K_2 (min ⁻¹)	R_2^2
CL-IL-TEOS-NH ₃	1.1912	0.2933	0.8833	1.2494	0.3314	0.9389

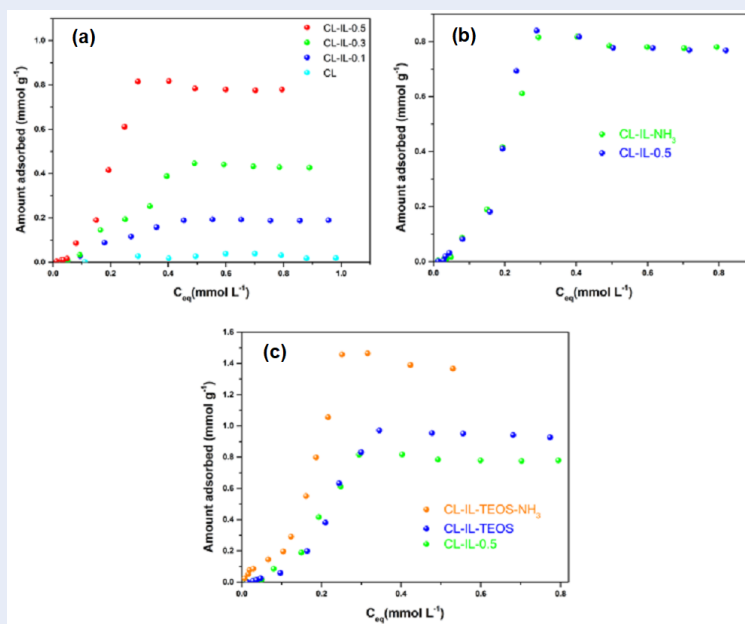


Figure 5: Comparison of sorption isotherms of MO onto the CL-IL materials: (a) CL; CL-IL-0.1; CL-IL-0.3 and CL-IL-0.5; (b) CL-IL-0.5 and CL-IL-NH₃ and (c) CL-IL-0.5; CL-IL-TEOS and CL-IL-TEOS-NH₃

CONCLUSIONS

CL-IL materials were successfully synthesized by silanization reaction of surface hydroxyl groups on cellulose and trimethoxysilane groups of the ionic liquid. The influence of reaction condition on the formation of CL-IL materials was investigated. High-efficiency modification of cellulose surface was obtained with the presence of agent coupling TEOS and NH₃. CL-IL materials are efficiency ion exchange material with fast sorption kinetic and high sorption capacity up to 1.4 mmol g⁻¹. Coupling agent TEOS displayed as a promising candidate for the silanization reaction of cellulose. This approach can be used for synthesis divers of functional cellulose materials, which can be aimed for the design of cheaper and high-efficient materials for catalysis, polymer composite, and adsorption in water treatment and depollution of industrial wastewater.

ABBREVIATIONS

CL: Cellulose
 FT-IR: Fourier-transform infrared spectroscopy
 IL: Ionic liquid
 MO: Methyl orange
 NMR: Nuclear magnetic resonance
 SEM: Scanning electron microscopy
 SIL: Supported ionic liquid
 TEOS: Tetraethyl orthosilicate
 TGA: Thermogravimetric analysis

COMPETING INTERESTS

The authors declare no competing interests.

AUTHORS' CONTRIBUTIONS

Ut Dong Thach designed the study and wrote the paper. Thi Lan Nhi Do and Ngoc Lan Anh Do conducted the experiments. Minh Huy Do helped to revise the manuscript.

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