Research Article

Lead Ions Removal Using Pineapple Leaf-Based Modified Celluloses

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Received: 8 March 2022; Revised: 9 April 2022; Accepted: 26 April 2022; Published online: 31 May 2022

Abstract
Pineapple leaves are largely discarded in the harvest area and considered as agricultural waste. Herein, the extracted pineapple leaves fiber was altered with chelating agents to become an adsorbent for lead ions (Pb^{2+}) removal from aqueous solutions. The initial investigation determined that the most appropriate conditions for extracting cellulose fiber from pineapple leaves were stirring at 90–100 °C in 10%w/v NaOH for 1 h. Next, carboxymethyl, amide, and amidoxime were used to modify with the extracted cellulose fiber, denoted as Cell-CMC, Cell-AM, and Cell-AMX, respectively. At pH 6, Cell-CMC, Cell-AM, Cell-AMX, and the extracted cellulose fiber had maximum adsorption potential values of 9.3, 1.5, 3.6, and 6.3 mg g^{-1}, respectively. In the kinetic analysis, Cell-CMC, Cell-AM, and extracted cellulose adsorption behaviors were well represented using a model of pseudo 1st order, while the adsorption behavior of Cell-AMX was best represented using a model of pseudo 2nd order. Further investigation demonstrated that the desorption efficiency of each adsorbent increased as the pH value was lowered from 3, 4, and 6.

Keywords: Adsorbent, Amide, Amidoxime, Carboxymethyl, Cellulose, Pineapple leaf fibers

1 Introduction

At present, pineapples are the third most popular fruit after bananas as well as citrus fruits, with approximately 25 million tons produced around the world [1]. Such massive amounts of pineapple production lead to high levels of agricultural waste products such as pineapple leaves (PAL). These leaves are usually composted or burned, which is a loss of potential natural fiber. The decomposition and burning of the leaves have also contributed to environmental pollution and the greenhouse effect. Therefore, the prospect of increasing the value of PAL is of interest.

Contamination of heavy metal ions in water, primarily sourced from industrial waste [2], is a major contributor to health problems and has become a global environmental concern. Heavy metals are not naturally decomposed and also can accumulate in crucial organs including the brain, kidney, and liver, leading to a variety of illnesses. For example, Pb is hazardous to the reproductive system, damages the brain, as well as causes kidney and liver disorders [3]. As a result, in compliance with implementation restrictions, several treatments and removing solutions have been established. As a modern technology, processes of adsorption treatment have gained considerable interest due to their simplicity, versatility, and efficiency [4], [5]. A variety of adsorbents have been utilized to eliminate harmful metal ions from wastewater [2]. Nonetheless, in recent years, researchers have focused on the search for a low-cost, commonly accessible adsorbent with technologically flexible and environmentally beneficial features [6]–[15].

Currently, there has been a lot of focus on the utilization of cellulose fibers obtained from various natural sources—wood sawdust [16], corncob [17], sugarcane bagasse [18], walnut shell [19], and PAL [20], [21]—as low-cost and environmentally friendly adsorbents for removal of harmful metal ions. Surface alterations have been proven in several investigations

to have a considerable impact on the adsorption capacity of unmodified or modified cellulose fibers for heavy metal ion removal. Because of the hydroxyl group's weak adsorption efficiency in cellulose fiber, different methods of cellulose modification have been used to boost its adsorption ability, such as modifying it with chelating groups with a stronger affinity to the targeted adsorbate [22]–[24]. Examples of the chelating groups that have been reported for modification with cellulose fiber and can increase its adsorption capacity are carboxymethyl [25], amidoxime [26], amide [27], iminodiacetic acid [28], and ethylenediaminetetraacetic [29]. The specific ability of these modified cellulosic adsorbents to adsorb metal ions depends heavily on the forms of the cheating group and metal ion, as well as the applied conditions [24], [30]–[39].

Recently, a few studies of PAL-extracted cellulose modifications with chelating groups have proved to be efficient cellulosic adsorbents for heavy metal ions removal. Heba *et al.*, studied the modified PAL-extracted cellulose using iminodiacetic acid [40]. When a 400 mg L^{-1} of lead ion concentration was used, the modified cellulose produced the maximum adsorption capacity of lead ions of 45 mg g^{-1}. Tangtubtim *et al.*, reported on PAL treated with alkali solution and immobilized with polyethyleneimine, achieving optimum maximum absorption capacities of Cu and Pb of 273 mg g^{-1} and 165 mg g^{-1}, respectively. Daochalermwong *et al.*, described the utilization of extracted cellulose from PAL that had been treated with ethylenediaminetetraacetic acid (Cell-EDTA) and carboxymethyl cellulose (Cell-CM) for removing lead and cadmium ions; they found that the optimum adsorption capacities for Pb^{2+} and Cd^{2+} were 41.2 mg g^{-1} and 33.2 mg g^{-1}, respectively, for Cell-EDTA and 63.4 mg g^{-1} and 23.0 mg g^{-1}, respectively, for Cell-CM [29]. The current study investigated the conditions for extracting cellulose fiber from PAL using an alkaline treatment by varying the extraction time and concentration of the aqueous solution of NaOH. Then, an extracted cellulose sample obtained from applying the optimized conditions was modified. Extracted cellulose fiber has low adsorption effectiveness due to its —OH group. With improved adsorption capacity, the —OH group of the obtained cellulose fiber can be transformed into the other functional group. Amide and amidoxime modified pineapple leaves-based cellulose have never been reported. Thus, amide, amidoxime, and carboxymethyl groups were explored in this study to be Cell-CMC, Cell-AM, and Cell-AMX, respectively. These modified celluloses as well as the unmodified extracted cellulose were subsequently employed to investigate Pb^{2+} removal in an aqueous solution as a representative of a heavy metal ion in wastewater. The subsequent study considered material characterizations as well as the kinetic behaviors of the modified and unmodified celluloses. In addition, a desorption experiment of Pb^{2+} on the modified celluloses was also carried out to decide whether they were suitable for use as practical adsorbents.

2 Experiment

2.1 *PAL composition analysis*

TAPPI standard test procedures were utilized to examine the PAL composition in terms of ethanol-benzene extractives, ethanol extractive, hot water extractive, holo-cellulose, hemicellulose, α-cellulose, lignin, and ash. The procedure has been reported elsewhere [28].

2.2 *Cellulose extraction from PAL*

Pineapple leaves were cut into little pieces and dried in an air oven (Labtech LD0-060E, UK) at 65 °C for an overnight period. After that, 1,000 mL of 5%, 10%, and 15% sodium hydroxide (NaOH, 98%, Carlo Erba, France) were used to extract PAL fiber from the dried sample (50 g) at 90–100 °C for 1, 2, and 3 h with continual stirring (SCILOGEX MS7-H550-s, USA). The obtained fiber was screened and carefully washed using tap water until the pH of the solution was neutral. The acquired fiber was then blended using a mechanical blending machine (Tefal, Ultrablend Boost BL985, France) and bleached by immersing the fiber in 50% sodium hypochlorite (NaOCl, available chlorine 4.00–4.99%, Sigma-Aldrich, USA) and storing it in a dark cabinet for 1 h at room temperature. The fiber was then carefully washed with tap water until the pH of the solution reached neutral before being bleached again at 70–80 °C for 30 min using 2 mL glacial acetic acid (CH_3COOH, 98.0%, QReC, New Zealand), 6 g of hypochlorite, and 640 mL of deionized water. To obtain the appropriate extracted cellulose fiber, it was washed until the pH of the solution reached neutral, then dried overnight at 65 °C in an air oven [29].

2.3 *Modifications of extracted PAL-cellulose fiber*

2.3.1. Carboxymethyl modification

Carboxymethyl cellulose (Cell-CMC) was made by combining extracted cellulose with a Sodium hydroxide (NaOH, 98%, Carlo Erba, France) solution (15%w/v) and iso-propanol (C_3H_8O, 99.7%, QReC, New Zealand) in a 1:4:20 (w/v/v) ratio of extracted cellulose:10% NaOH solution: iso-propanol. After that, the mixture was stirred for 1 h at room temperature. Next, sodium monochloroacetate ($C_2H_2ClO_2Na$, 98%, Sigma-Aldrich, USA) was added to the solution at a ratio of extracted cellulose:$C_2H_2ClO_2Na$ of 1:1.2 (w/w), and the temperature was raised to 55 °C and left for 3 h. The solution was then neutralized with 90% acetic acid (CH_3COOH, 98.0%, QReC, New Zealand), and subsequently washed 4 times with ethanol solution (CH_3CH_2OH, 70%, Sigma-Aldrich, USA) (70%, v/v). Finally, the synthesized Cell-CMC was placed in an open container and allowed to dry overnight at room temperature before being used as an absorbent [24].

2.3.2. Amide modification

The amide cellulose (denoted as Cell-AM) was synthesized by mixing 0.8 g of extracted cellulose and 200 mL of deionized water in a flask. The cellulose was then mixed with acrylamide solution ($CH_2CHCONH_2$, 98%, Sigma-Aldrich, USA) (0.28 mol) and cerium(IV) sulfate ($Ce(SO_4)_2$, ≥ 99.99%, Sigma-Aldrich, USA) (1.23 mmol) and stirred at room temperature for 24 h. All of the preparatory procedures were carried out in a nitrogen atmosphere. After that, the cellulose was rinsed 6 times with tap water before being mixed with acetone (C_3H_6O, 99.5+%, Alfa Aesar, USA) and stirred for 5 min. Finally, the modified cellulose was dried for 24 h in an air oven at 40°C before being utilized as an absorbent [26].

2.3.3. Amidoxime modification

The preparation of amidoxime cellulose (denoted as Cell-AMX) was divided into two steps: cyanoethylation and amidoximation. For cyanoethylation, 0.36 g of extracted cellulose was combined with 40 mL of 1 M sodium hydroxide under constant stirring for 7 h to allow the extracted cellulose to dilate. The solution was then gradually added to 2 mL of acrylonitrile (C_3H_3N, ≥ 99%, Sigma-Aldrich, USA) and agitated for another 12 h. Following the completion of the reaction, 30 mL of concentrated iso-propanol was used to dissolve any unreacted acrylonitrile, which was then rinsed with deionized water. For amidoximation, the cellulose from the first step was mixed with hydroxylamine hydrochloride ($HONH_2$.HCl, 98%, Sigma-Aldrich, USA) and NaOH using a mole ratio of 1:1 at 50 °C and stirred for 10 h. The synthesized modified cellulose was dried in the oven at 70 °C for 4 h before being used as an absorbent [25].

2.4 *Material characterization*

The functional groups of the samples were determined using a Fourier-Transform Infrared Spectrometer (FT-IR, model: Bruker Optics, ALPHA-E, attenuated total reflection (ATR) mode).

Images of the sample's morphological, physical, and chemical components were acquired using a scanning electron microscope integrated with an electron dispersive X-ray spectrometer (SEM-EDS, model: JEOL JSM7600F). The samples were coated with platinum before imaging.

2.5 *Adsorption and kinetic models studies*

To assess the adsorption effectiveness of the modified cellulose samples, different Pb^{2+} concentrations ($Pb(NO_3)_2$, 99.5%, QReC, New Zealand) in DI water were used. The kinetic models of adsorption (pseudo 1st and pseudo 2nd) were identified by using each sample (0.5 g) to adsorb 100 mg L^{-1} of Pb^{2+} for different times (0–20 min for Cell-CMC, 0–15 min for Cell-AM 0–180 min for Cell-AMX, and 0–20 min for extracted cellulose). Each kinetic model of adsorption was developed utilizing data from the experiments. Non-linear fitting analyses were performed to obtain the kinetic parameters. For desorption efficiency, each modified cellulose was utilized to adsorb 100 mg L^{-1} of Pb^{2+} until the equilibrium time was reached. Then, the sample was immersed in a hydrochloric acid (HCl, 37%, Sigma-Aldrich, USA) solution at pH levels of 3.0, 4.2, and 6.0 for 90 min. Each mixture was filtered to remove the modified sample and the Pb^{2+} concentration of each residual solution was finally determined. In all of the studies, the amounts of Pb^{2+} were measured using an atomic absorption spectrometer (AAS, Perkin Elmer, HGA-800) [29].

3 Results and Discussion

3.1 *Analysis of PAL composition*

Table 1 demonstrates the composition of different components of the dried PAL, which were determined by the TAPPI standard methods [29] (Details are provided in the supporting information). The total contents of lignin and extractives (wax, fat, pectin, tannin, and oil) were approximately 14% and 30%, respectively. The contents of α-cellulose and hemicellulose were 40.0% and 16.8%, respectively, meaning the content of holocellulose was 56.8% and the content of α-cellulose was 70.4% of the holocellulose. This high content of α-cellulose from the PAL was desired for use in the modifications with the CMC, AM, and AMX groups, and then for utilization as heavy metals ion adsorbents. However, before the modifications, suitable conditions for the extraction of α-cellulose from dried PAL had to be determined, as described in Section 3.2.

Table 1: Composition of components of dried PAL determined using the TAPPI standard methods

Component	Amount (%w/v)
Ethanol+Benzene extractive	13.1
Ethanol extractive	7.1
Hot water extractive	9.3
α-Cellulose	40.0
Hemi-cellulose	16.8
Lignin	13.9

3.2 *Cellulose extraction from PAL*

Table 2 shows the weight of cellulose and the cellulose yield obtained from the cellulose extraction of dried PAL using different concentrations of NaOH (5, 10, and 15%w/v) and different extraction times (1, 2, and 3 h) using 50 g of dried PAL in each batch. It was found that increases in either the NaOH concentration or the extraction time tended to lower the cellulose yield. The highest yield of cellulose of 13.4% (6.7 g from dried PAL 50 g) was obtained at 5%w/v NaOH after 1 h of extraction. However, the quality of the extracted cellulose from each batch was analyzed using SEM (Figure 1), which revealed that although the extracted cellulose with 5%w/v NaOH had the highest cellulose yield, the quality of the sample was the lowest due to agglomeration of the fibers [Figure 1(a)]. This

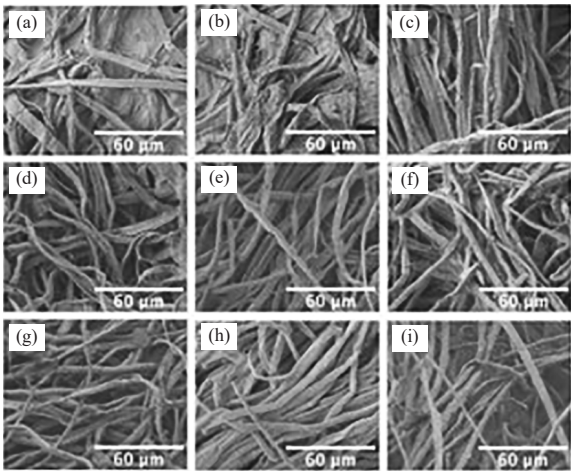

Figure 1: SEM images of the cellulose obtained from cellulose extraction from dried PAL using different NaOH concentrations and extraction times: (a) 5% NaOH, 1 h, (b) 5% NaOH, 2 h, (c) 5% NaOH, 3 h, (d) 10% NaOH, 1h, (e) 10% NaOH, 2 h, (f) 10% NaOH, 3 h, (g) 15% NaOH, 1 h, (h) 15% NaOH, 2 h, (i) 15% NaOH, 3 h.

Table 2: Weight of cellulose yield obtained from NaOH extraction using different concentrations and times

NaOH Concentration (%w/v)	Extraction Time (h)	Weight of Cellulose (g)	Cellulose Yield (%)
5	1	6.7	13.4
	2	6.1	12.2
	3	5.8	11.6
10	1	5.6	11.2
	2	5.2	10.4
	3	4.4	8.8
15	1	4.7	9.4
	2	4.7	9.4
	3	4.4	8.8

could have been because of insufficient concentration of NaOH so there was an incomplete reaction with the compatibilizing agent (lignin) between the fibers and this caused the agglomeration of the fibers. Similarly, the quality of the sample in Figure 1(b) was unacceptable due to incomplete extraction. The other samples [Figures 1(c)–(i)], all of them have a suitable length with an approximate diameter of 7–10 µm and no non-fibrous particles were observed. Nonetheless, the sample from 10%w/v NaOH for 1 h had the highest yield among these good quality fibers. The higher concentrations of NaOH and the longer times could hydrolyze the cellulose and subsequently, the yields

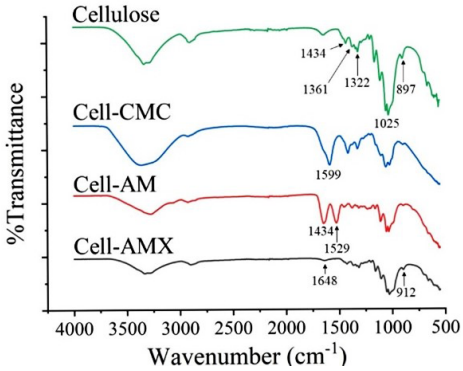

Figure 2: FTIR spectra of extracted cellulose, Cell-CMC, Cell-AM, and Cell-AMX.

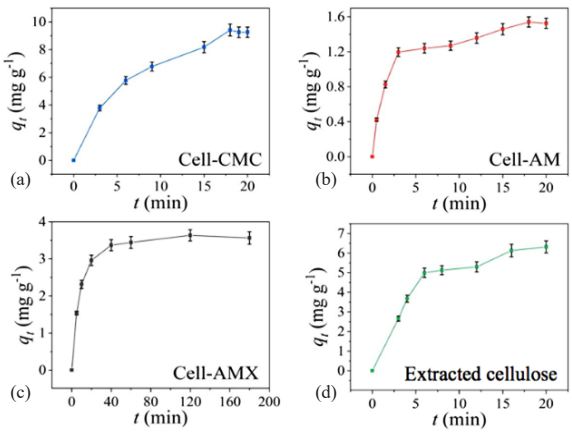

Figure 3: Effect of contact time for Pb^{2+} on: (a) Cell-CMC, (b) Cell-AM, (c) Cell-AMX, and (d) extracted cellulose. Conditions for adsorption: pH 6, room temperature, concentration of Pb^{2+} = 100 mg L^{-1}.

steadily decreased. Hence, the use of 10%w/v NaOH for 1 h was considered the most reasonable condition for extracting cellulose from dried PAL.

3.3 *Analysis of extracted and modified celluloses*

To increase the heavy-metal ion adsorption capacity of the extracted PAL cellulose, the extracted cellulose was functionalized with CMC, AM, and AMX groups using the selected extraction conditions; these three modified cellulose types were called Cell-CMC, Cell-AM, and Cell-AMX, respectively. The FTIR spectra of the three modified cellulose types compared with that of the extracted cellulose are illustrated in Figure 2. The –OH stretching vibration mode was assigned to the broad peak seen about 3,600–3,200 cm^{-1} in the extracted cellulose, whereas the C–H stretching vibrational mode was assigned to the band around 2890 cm^{-1}. The bending and stretching vibrations in the cellulose backbone of $–CH_2$, –CH, C–O, and –OH bonds were represented by the bands at 1,434, 1,361, 1,322, 1,025, and 897 cm^{-1} [41]. The –OH stretching vibrational mode was suggested by the large absorption band at 3,390 cm^{-1} for Cell-CMC. The –CH stretching of CH_2 and CH_3 groups in the CMC structure caused the band at 2,962 cm^{-1}. The strong absorption band at 1,599 cm^{-1} specified the presence of the carboxyl group (–COO–), proving that the hydroxyl group on cellulose had been successfully substituted with a carboxymethyl group. The bands at 1,329 cm^{-1} and 1,418 cm^{-1} were determined to be the –OH bending vibration mode and $–CH_2$ scissoring, respectively. The band at 1,063 cm^{-1} belonged to the CH–O–CH_2 stretching vibration mode [42]. For Cell-AM, the success of amidation was confirmed by the disappearance of hydroxyl groups and the emergence of the amide group, specified by the bands at 1,650 cm^{-1} for the C=O stretching vibration mode and 1,529 cm^{-1} for the C–N stretching and N–H deformation vibration modes [26]. The existence of the AMX group on the cellulose backbone was identified by a band at 1,648 cm^{-1} for the stretching vibration mode of C=N and at 912 cm^{-1} for the stretching vibration mode of N–O in Cell-AMX [43].

3.4 *Adsorption and kinetic models studies*

3.4.1 Effect of contact time

Cell-CMC, Cell-AMX, and Cell-AM, these four samples were used to adsorb 100 mg L^{-1} of Pb^{2+} for various times to determine the effect of contact time on Pb^{2+} adsorption by extracted cellulose. It should be emphasized that all of the tests in this section were conducted at pH 6 and the adsorption capacity against time was plotted, as shown in Figure 3. The adsorption efficiency of Cell-CMC was substantially larger than that of the unmodified cellulose, whereas the Cell-AMX and Cell-AM, unfortunately, provided a weak adsorption efficiency than the unmodified cellulose. The maximum adsorption efficiency of the Cell-AM for Pb^{2+} was the lowest among all the samples at 1.5 mg g^{-1} followed by Cell-AMX at 3.6 mg g^{-1}. The

maximum adsorption efficiency was 6.3 mg g^{-1} for cellulose, while Cell-CMC had the highest adsorption efficiency at 9.3 mg g^{-1}. In Figure 3, it is also clear that these modified celluloses reached their maximum adsorption efficiency close to unmodified cellulose (within about 17 min except for Cell-AMX). These findings may be explained by the fact that the carboxymethyl possesses the strongest electron-donating group among these four functional groups, so Cell-CMC had the highest adsorption efficiency. Another interesting finding was that the adsorption efficiencies of Cell-CMC for Pb^{2+} were significantly higher than those of the functional groups containing a nitrogen atom—Cell-AM and Cell AMX—. It could be explained by the fact that the metal ion or adsorbate has a high electronegativity, in which case the effects of bond formation through ionic bonding, which required less energy, could be prominent. As a result, Pb^{2+} adsorption on Cell-CMC is more effective than nitrogen group modified cellulose, where metal ion adsorption occurs via covalent interaction. In addition, the functional groups containing a nitrogen atom were perhaps protonated at this mild acidic level (pH 6). Thus, Cell-AM and Cell AMX had adsorption efficiency values lower than those for Cell-CMC and the extracted cellulose.

3.4.2 Kinetic models for Pb^{2+} adsorption onto Cell-CMC, Cell-AM, and Cell-AMX

To evaluate the adsorption kinetic behavior of Pb^{2+} onto Cell-CMC, Cell-AM, or Cell-AMX, the following steps were performed. First, from the plots between the adsorption efficiency (q_t) and time (t) shown in Figure 3, a scatter plot was made of qt and t using the OriginPro software package. Second, the software was used to fit a non-linear curve of q_t and t values by fitting them with a pseudo 1st order model [Equation (1)] or a pseudo 2nd order model [Equation (2)] [29], as shown below.

$$q_t = q_1(1-\exp(-k_1 t)) \quad (1)$$

$$q_t = \frac{t}{(1/k_2 q_2^2) + (t/q_2)} \quad (2)$$

where q_1 and q_2 are the amount of Pb^{2+} (mg g^{-1}) at equilibrium, q_t is the amount of Pb^{2+} (mg g^{-1}) at time t (min), and k_1 and k_2 are rate constants. Third, use the OriginPro software package to determine the values of q_1, k_1, q_2, and k_2. Fourth, calculate statistical information, namely the adjusted determination coefficient (R^2_{adj}), the coefficient of determination (R^2), the error sum of squares (SSE, as expressed in Equation (3), and Akaike's Information Criterion (AIC, as expressed in Equation (4)) [29].

$$SSE = \sum_{i=0}^{N} (q_{t,cal(i)} - q_{t,exp(i)})^2 \quad (3)$$

$$AIC = N\left(\frac{SSE}{N}\right) + 2N_p + \frac{2N_p(N_p+1)}{N-N_p-1} \quad (4)$$

where N represents the number of data points. The number of Pb^{2+} at each data point are $q_{t,cal}$ and $q_{t,exp}$; obtained from the calculation regarding non-linear fitting and the experiment, respectively. N_p is the number of parameters in the model. Fifth, analyze the statistical values in the fourth step to evaluate which model has the better fit for the experiment results. The results are illustrated in Figure 4 and Table 3.

Several important pieces of information can be observed from the results in Figure 4 and Table 3. First, all the maximum adsorption efficiencies obtained from the pseudo 2nd order model (q_2) were slightly larger than those obtained from the pseudo 1st order model (q_1). Second, all the values of both R^2 and R^2_{adj} of each pseudo 2nd order model were slightly larger than those of each pseudo 1st order model. This implied that perhaps the pseudo 2nd order model offered the best fit with the experimental data [44]. However, both values of R^2 and R^2_{adj} alone cannot be utilized to precisely decide which model best suited the experimental data [40]; thus, both values of SSE and AIC must be introduced here in order to make the final decision. The model with an SSE value closer to zero and a lower AIC value would be the best model to represent the experimental data, according to SSE and AIC conventions. The SSE and AIC values of the pseudo 1st order model were much lower than those of the pseudo 2nd order model for Pb^{2+} adsorptions onto Cell-CMC, indicating that the pseudo 1st order model was a superior fit to the experimental data. Third, the SSE and AIC values of Cell-AM in the pseudo 1st order model were much lower than those in the pseudo 2nd order model. This also means that the pseudo 1st order model fit the experimental data better. Fourth, the SSE and

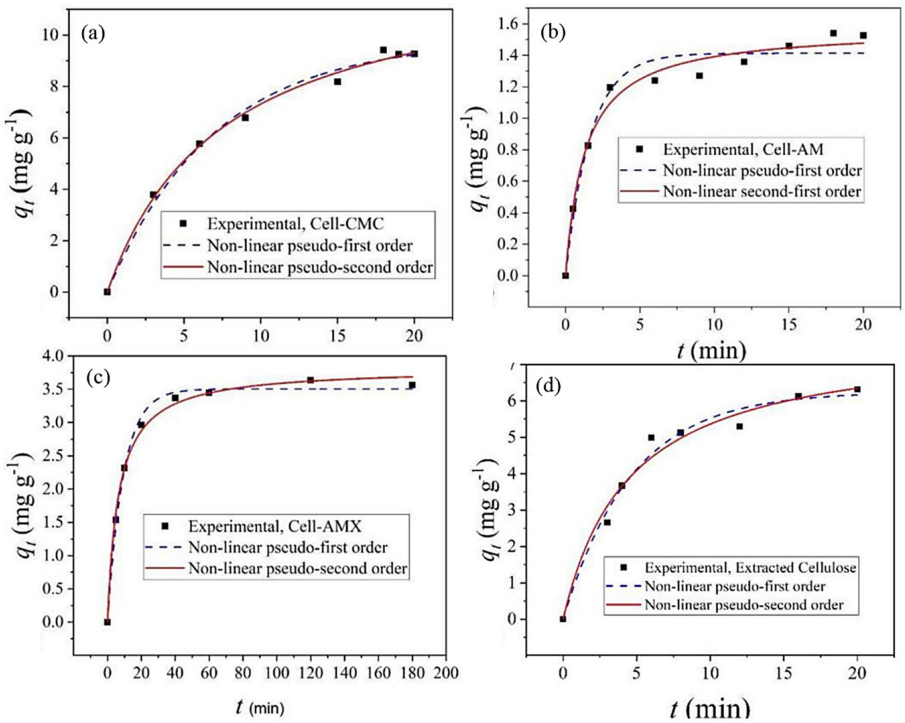

Figure 4: Plots of non-linear pseudo 1st order and non-linear pseudo 2nd order kinetic models for the Pb^{2+} adsorption onto (a) Cell-CMC, (b) Cell-AM, (c) Cell-AMX, and (d) extracted cellulose.

Table 3: Parameter values in the pseudo 1st and 2nd order models for Cell-CMC, Cell-AM, and Cell-AMX

Absorbent, Model	Parameter					
	q_1 or q_2 (mg g^{-1})	k_1 or k_2 (min^{-1})	R^2	R^2_{adj}	SSE[(a)] (%)	AIC[(b)]
Cell-CMC, Pseudo 1st order	9.78	0.1442	0.9920	0.9906	3.51	9.91
Pseudo 2nd order	12.84	280.0761	0.9955	0.9948	9.35	15.75
Cell-AM, Pseudo 1st order	1.41	0.5945	0.9685	0.9646	0.90	6.90
Pseudo 2nd order	1.57	2.9709	0.9850	0.9831	0.93	6.93
Cell-AMX, Pseudo 1st order	3.50	0.1063	0.9951	0.9943	0.05	10.05
Pseudo 2nd order	3.82	8.4563	0.9962	0.9956	0.03	10.03
Extracted Cellulose, Pseudo 1st order	6.25	0.216	0.9814	0.9784	0.58	16.58
Pseudo 2nd order	7.78	104.3497	0.9962	0.9956	0.66	16.66

[(a)] SSE (%) = sum of squares error, [(b)] AIC = Akaike's Information Criterion

AIC values of Cell-AMX in the pseudo 2nd order model were just slightly lower than those in the pseudo 1st order model, indicating that the pseudo 2nd order model would better fit the experimental data. Finally, the SSE and AIC values of the extracted cellulose in the pseudo 1st order model were marginally lower than those in the pseudo 2nd order model, suggesting that the pseudo 1st order model fit the experimental data better. In summary, Cell-CMC, Cell-AM, and extracted cellulose followed a pseudo 1st order model, while Cell-AMX followed a pseudo 2nd order model under the conditions conducted in this work. The

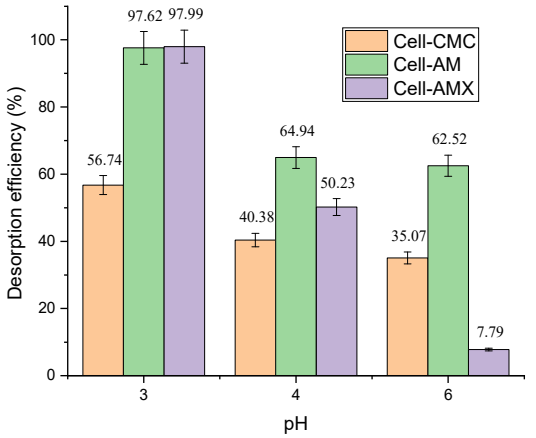

Figure 5: Effect of pH on desorption of CMC-Cell, Cell-AM, and Cell-AMX.

difference in the kinetic models of Cell-AMX which is a pseudo 2nd order model from others is perhaps due to the difference in the adsorbent type or the adsorbate concentration. It can be seen in Figure 3 that the cell-AMX reached its adsorption slower than others follow by the fact that the fit of the model to the pseudo 2nd order kinetics is better when adsorbate concentration is not high [45].

3.5 *Desorption studies of Cell-CMC, Cell-AM, and Cell-AMX*

A varying pH desorption test (using pH 3, 4, and 6) was performed to check the desorption capacity of the modified celluloses. Figure 5 depicts the correlation between pH and the modified celluloses' desorption efficiency, where the desorption efficiency was calculated using Equation (5):

$$\text{Desorption efficiency (\%)} = \frac{A_d}{A_a} \cdot 100 \quad (5)$$

Where A_d represents the quantity of metal ion desorbed and A_a represents the quantity of metal ion adsorbed.

The results demonstrated that the desorption efficiency of every adsorbent increased as the pH values decreased. This can be explained by putting into consideration the surface charge. Because H^+ competes with Pb^{2+} for adsorption on the surface's adsorbent, the combination of Pb^{2+} with modified cellulose types is more unstable. As a result, the desorption efficiency decreases. Furthermore, Figure 5 demonstrates this as well that the order of desorption efficiency was Cell-AMX ≈ Cell-AM > Cell-CMC at pH 6, which could have been due to the stronger adsorption between the CMC group and Pb^{2+}, so that it was more difficult to release the adsorbate from the surface of Cell-CMC.

4 Conclusions

The most suitable NaOH concentration and extraction time to extract cellulose fiber from pineapple leaves were 10%w/v NaOH and 1 h, respectively. The extracted pineapple fibers were then modified using carboxymethyl, amide, or amidoxime groups to obtain CMC-Cell, Cell-AM, and Cell-AMX, respectively. All of the modified celluloses were successfully synthesized and utilized as adsorbents to investigate the removal of Pb^{2+} from aqueous solutions. The results showed that Cell-CMC had the highest Pb^{2+} absorption at 9.3 mg g^{-1}, which was greater than that of unmodified cellulose at 6.3 mg g^{-1}, while Cell-AM and Cell-AMX had considerably lower adsorption efficiencies at 1.5 and 3.6 mg g^{-1}. These adsorbents exhibit lower adsorption efficiency than other adsorbents with the same functional group, which might be related to differences in the number of active sites per weight of the adsorbents. In the kinetic study, Cell-CMC, Cell-AM, and extracted cellulose followed a pseudo 1st order model, while only Cell-AMX followed a pseudo 2nd order model. The difference among the kinetic models that described the adsorption behavior of each adsorbent-adsorbate system could have resulted from differences in the adsorbate concentrations or the adsorbent types. A desorption study of all the modified celluloses was also conducted and it was found that increases in the pH resulted in lowering the desorption efficiency, which resulted from decreases in the availability of protons. This study demonstrated that pineapple leaves as agricultural waste, can be transformed into adsorbents and that Cell-CMC has a high potential for practical uses in heavy metal adsorption of wastewater.

Acknowledgments

This research is funded by Kasetsart University through the Graduate School Fellowship Program and the Kasetsart University Research and Development Institute (KURDI), Bangkok, Thailand.

Author Contributions

T.S.: conceptualization, data curation, investigation, reviewing, editing; S.C.: reviewing, editing; S.R., C.N., and P.P.: conceptualization, reviewing, and funding acquisition; A.S.: conceptualization, writing—reviewing and editing, funding acquisition, project administration. All authors have read and agreed to published this version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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