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Application of Amberlite and magnetic ion-exchange resins for dissolved organic matter removal in sugar mill effluent

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Abstract

This study investigated the viability of using MIEX® GOLD (MIEX®) and AMBERLITETM FPA98 Cl (AR) ion-exchange resins to remove dissolved organic carbon (DOC) from sugar mill effluent (SME) in laboratory-scale experiments; effects of resin dose contact time and pH on DOC removal were also investigated. Sorption kinetics of both resins were fitted to pseudo-second orders and then to pseudo-first orders, while equilibrium sorption was fitted to the Freundlich isotherm. The initial rate constant and sorption capacity were higher for MIEX[®] (0.31 mLmg⁻¹min⁻¹ and 0.33 mg/mL) than for AR (0.09 mLmg⁻¹min⁻¹ and 0.23 mg/mL). The 5 mL/L dose of MIEX® with a contact time of 20 min removed 54.82 % of the DOC; the 5 mL/L dose of AR removed the same amount of DOC with a contact time of 60 min. Through non-targeted analysis, both resins selectively removed carbohydrate-like, lignin-like, and condensed aromatic structure DOM with more oxidized characters. A pretreatment with MIEX® or AR, followed by FeCl³ coagulation/sedimentation, not only reduced 87.5 % of the coagulant demand but also removed higher amounts of DOC and UV²⁵⁴ compared to FeCl3 coagulation/sedimentation alone. Both resins have potentials as a pretreatment for enhanced coagulation processes to reclaim SME.

Keywords: MIEX resin, Amberlite resin, Coagulation, Dissolved organic matter, Ion-exchange

1. Introduction

Thailand is one of the top five of the largest sugar cane producers in the world. Normally, industrial sugar cane production requires large amounts of water and releases equally large amounts of effluent, which is high in dissolved organic matter (DOM) [1]. Over the past couple of years, Thailand has encountered serious drought and shortages in source water for agricultural, domestic, and industrial uses [2]. Due to quality of effluent, it is stored and reuse only for agricultural purpose around the factory. Reusability of effluents for other purposes is highly depended on its quality. Hence, further treatment of effluents to increase its quality would be increasingly attractive for other resus purposes ensure production during serious drought. With proper wastewater reclamation processes, recycled wastewater could be a viable option for the sugar industry.

Conventional wastewater treatments are typically not capable of removing all organic matter and achieve the water quality standard necessary for reuse. DOM in treated wastewater has become problematic because of aesthetic concerns, like odor, color, and taste, or undesirable health effects associated with disinfection by-products [3]. Organic matter is difficult to treat due to its recalcitrant nature. After treatment, effluent wastewater from sugar mills still has a yellowish color and high level of DOM, measured as dissolved organic carbon (DOC). As a result, the treated effluent becomes objectionable for reuse. Based on the structure of DOM, many advanced treatment processes have been applied to remove DOC from wastewater including sorption, ion-exchange, precipitation, advanced oxidation processes, and membrane separation. In many cases, processes were combined [4]. DOC is one of the main constituents that commonly remains in treated effluents, so treatment processes must be able to efficiently remove DOC. Anion-exchange resins have been one of the more effective processes for removing negatively charged DOM. This process can remove a wide range of DOM, thus providing high DOC removal, can be adapted to different reactor designs, and can be operated continuously or periodically [5]. In addition, the application of anion-exchange resins before the coagulation/sedimentation process decreased coagulant demand and provided greater DOC removal [6].

Recently, the application of magnetic ion exchange resin (MIEX[®]) to remove organic or inorganic matter from water has garnered attention from researchers as a response to problems with organic matter removal. The MIEX® has many advantages: magnetic properties, small pore size, high density, and a high settlement rate due to magnetized iron oxide in the polymer matrix, which allow for greater external surface area that provides rapid sorption and a recovery rate 99.9% [7]. Pre-treatments with MIEX®, could significantly enhance the efficiency of coagulation processes for DOM removal; MIEX® resin can be effectively regenerated over multiple regeneration cycles and previous study showed effective regeneration over 11 cycles [5, 8-10]. MIEX[®] has been successfully applied in surface water treatment and wastewater reclamation [11, 12]. However, its applications for industrial wastewater reuse,

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particularly in the sugar industry, have not been explored. Recently, MIEX® GOLD has been developed and has never been used for DOC removals sugar mill effluent treatment for water reclamation.

In this study, laboratory-scale experiments were used to determine the applicability of an MIEX® GOLD resin (MIEX®) in removing DOC from sugar mill effluent (SME). An AMBERLITETM FPA98 Cl resin (AR), an anion-exchange resin used in refined sugar production, was also used for DOC removal. It was specially designed for the decolorization of highly organic colored liquid sugar syrups. It can be effectively regenerated approximately 4-6 cycles [13-15]. Isotherms and kinetics for both resins, saturation in multiple-loading experiments, and the effects of MIEX® pre-treatment prior to coagulation/sedimentation processes on coagulant demand were investigated. We also investigated molecular DOM removal by both resins using non-targeted analysis via Orbitrap mass spectrometry.

2. Materials and methods

2.1 Water sampling and analyses

Water samples were collected from a storage pond containing both natural river water mixed with secondary effluent from a sugar mill in northeastern Thailand in August 2020. In total, 200 L of water samples were used throughout the experiments. The water samples were analyzed for pH, turbidity, color (ADMI Standard Method Spectrophotometer Hach, DR6000), DOC concentration (Standard Method 5310B Total Organic Carbon by multi N/C 2100S, Analytik Jena, Germany) and UV absorbance at 254 nanometers (UV254; Spectrophotometer Hach, DR6000)

2.2 Coagulation/sedimentation experiment

Samples underwent coagulation using ferric chloride (FeCl36·H2O) AR grade at 10-300 mg/L to test for the optimal dosage. The jar test experiment was conducted using 1 L of SME sample (A Phipps & Bird PB-700 jar tester). The jar test involved 1 min at 200 rpm for rapid mixing, 30 min at 40 rpm for slow mixing, and 30 min at rest for let sample settling. Supernatant was collected and filtered through a syringe filter (0.45 µm nylon syringe filter, MS). Filtrate was analyzed for color, DOC, and UV254.

2.3 Ion-exchange resins for DOC removal

Two anion-exchange resins, MIEX® GOLD (IXOM Watercare, Inc., Australia) and AMBERLITETM FPA98 Cl (Dupont, Inc. obtained from Sugar Company), were used for water treatment experiments. AR is a resin used in white sugar production to remove color; MIEX[®] is widely used for water treatment. Both resins used in this study were new. By SEM images in previous reports, MIEX[®] has a uniform opaque bead size of 180-250 μ m [16, 17] while AR has average bead size of 500 μ m [18]. The characteristics of MIEX[®] and AR showed at Table 1 (IXOM Watercare, Inc. and Dupont, Inc.) Both resins were stored in deionized water and then rinsed with deionized water before further experiments were conducted.

Table 1 Characteristics of MIEX® and AR

2.4 Single batch resin experiment

2.4.1 Kinetics

The sorption experiments were carried out in 2-liter glass beakers and aimed to investigate suitable operational conditions for resin dose and contact time, to be used in later experiment. During these tests, 5, 10, 15, 20, and 25 mL of each resins were added to 1 L of effluent water, which was stirred continuously stirred in a jar test reactor. The resins were mixed with the water sample at for 60 min at 200 rpm. After allowing the resin to settle for 30 min, supernatant was collected and filtered for DOC and UV²⁵⁴ analysis. The optimal dosage was obtained based on the efficiency of the DOC and UV254 removal for each resin dosage. The kinetic test was performed at the optimal resin dosage; treated water samples were taken at 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70, 80, 90, and 120 min for DOC measurement. The kinetic models can be expressed by the pseudo-first-order (Eq. (1)) and the pseudo-second-order (Eq. (2)) kinetic models, and the initial sorption rate constant can be obtained from Eq. (3):

$$
h = \mathbf{k}_2 \longrightarrow \mathbf{qe}_e^2 \tag{3}
$$

where $q_e(\text{mgmL}^{-1})$ and $q_t(\text{mgmL}^{-1})$ are the adsorbed DOC amounts at equilibrium and at time *t* (min), respectively; $k_l(\text{min}^{-1})$ and k_2 $(mLmg^{-1}min^{-1})$ are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively; *h* (mgmL⁻¹min⁻¹) is the initial sorption rate.

2.4.2 Isotherm models

The equilibrium data were fitted by two isotherm models, the Langmuir (Eq.(4)) and Freundlich (Eq.(5)) models:

$$
\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}k_L}
$$
\n
$$
\log q_e = \frac{\log C_e}{n} + \log k_F
$$
\n(4)

where *qmax* (mg/mL) is the theoretical maximum DOC adsorbed, and *k^L* (mL/mg) is the Langmuir model constant, while 1/ n and *k^F* (mL/mg) are the Freundlich intensity parameter and the capacity factor, respectively. The correlation coefficient (R^2) was used to assess the validity of the isotherm models in this study.

2.4.3 Effects of pH on DOC removal

The influences of initial pH on the sorption of both resins was investigated; initial pH values ranged from 7 to 9. This range was selected based on deviations in actual effluent pH. A resin dose of 10 mL/L and a contact time of 60 minute were used. Solutions of 0.1 N NaOH or 0.1 N HCl were used to adjust the initial pH of each water sample.

2.4.4 Multiple - loading tests

A multiple-loading test was conducted using resin doses in the range of typical resins for ion-exchange processes. From the results of the sorption kinetic experiments, 5 mL/L dose was selected for both resins, and a 60-minute contact time was used for all of the multiple-loading tests to ensure the equilibrium of both resins. First, 1 L of water sample was added to the resins with a loading of 200 BV; the sample was mixed for 60 min and then allowed to settle for 30 min. The supernatant was taken for DOC and UV254 analysis. The experimental procedure was repeated until 6000 BV was reached.

2.5 Changes of molecular DOM by non-targeted analysis using Orbitrap mass spectrometry

The amount of DOC in 1 L of each water sample was measured before and after treatment by MIEX[®] or AR using solid phase extraction and a Bond Elut PPL cartridge (Agilent Technologies, CA, USA). Extraction procedures are described in [19]. In brief, the water samples were filtered through a glass fiber filter (GF-75, Advantec Toyo Kaisha, Tokyo, Japan) before being adjusted to a pH of 2 with HCl. The water samples were passed through the cartridge by vacuum at –10 mmHg, and DOM was eluted by 10 mL of methanol (LC-MS grade). The extracts were stored at –20 °C before the non-targeted analysis. The extracts were analyzed by Orbitrap mass spectrometry (Q Exactive Plus, Thermo Fisher Scientific, Walham, MA, USA) at the Synchrotron Light Research Institute in, Thailand, using a flow injection mode and a negative-ion full scan mode with a mass to charge range of 100-1000. Other analytical conditions are described in [20, 21]. Molecular formula identification was processed by compound identification algorithms [22, 23] that considered the number of elements as follows: C_{0-39} , H_{0-72} , O_{0-20} . The formulae assigned in this study followed 7 Golden rules [24] and ranged in degree of unsaturation [25] to ensure DOM formula identification. Changes to the molecular DOM formulae were described in a semiquantitative approach developed by [21] Molecular characteristics, such as the Van Krevelen diagram [26],were calculated from number of atoms; the carbon oxidation state (C_{os}) [27] was calculated using Eq.(6); and the degree of unsaturation (DBE–O)/C [28] was calculated using Eq. 7:

$$
C_{OS} = (H - 20)/C \tag{6}
$$

 $(DBE - 0)/C = [1 + 0.5(2C - H) - 0]/C$ (7)

3. Results and discussion

3.1 Effluent water characteristics

The characteristics of the SME are summarized in Table 2. The effluent water sample had a pH values of 7.95, high turbidity (12 NTU), a light yellow color (16 ADMI), high organic content (7.37 mg/L DOC), high UV254 absorbance (0.1625 cm⁻¹), and low specific ultraviolet absorbance (SUVA; 0.022 Lmg⁻¹cm⁻¹). The physical appearance of the water samples was highly turbid, and slightly yellow.

Table 2 Characteristics of the SME

3.2 DOM removal by MIEX® and AR resins

3.2.1 Effect of MIEX® and AR dosage on DOC removal

The effects of MIEX[®] and AR dosage on DOC removals were determined by varying the doses from (5, 10, 15, 20 and 25 mL/L) and maintaining a contact time of 60 min. Figure 1 illustrates the DOC removal efficiency of both resins.

Figure 1 DOC Removal efficiency for MIEX[®] and AR at different doses after a 60-minute contact time

The 5 mL/L dose of both MIEX® and AR was found to remove the most DOC per unit of resin used, at 54.82 % and 53.93%, respectively. Increasing the MIEX® and AR doses from 5 mL/L to 25 mL/L increased the total percent of DOC removed from 55% to 65%. However, considering the percent of DOC removed per mL of resin used, DOC removal decreased as resin dosage increased for both resins. The 5 mL/L dosage was selected for the kinetic experiments for both of resins and was recommended as the operating parameters for DOC removal from SME. The DOC removal of $\text{MIEX}^{\circledcirc}$ and AR in this study were slightly greater than $\text{MIEX}^{\circledcirc}$ resins (approximately 8-44%) [29] and other anion resins (approximately 23-41%) [30] that has been reported in previous studies for water treatment.

3.2.2 Kinetics

The contact time required to reach sorption equilibrium is an important consideration for the design and operation of the system. Figure 2 summarizes DOC removal for different contact times for both resins. The amount of DOC adsorbed by MIEX® and AR increased with contact time. The sorption of DOC by MIEX® and AR increase sharply in the first 15 min. This likely because surface sites are available during the first 15 min. After a subsequent 20 min, the DOC sorption on both resins increased slightly. This implies repulsive forces from of molecules adsorbed on the resin with the solute molecules [31, 32]. After 30 min for MIEX® and 60 min for AR, minimal adsorptions was observed, implying the sorption equilibria for DOC on MIEX® and AR. Based on these results, the optimum contact time for 20 min for MIEX® and 60 min for AR. In order to ensure equilibrium sorption of DOC for both resins, the following equilibrium isotherm experiments had a contact time of 60 min.

Sorption kinetics explain the removal efficiency of sorbate on sorbent as time passes (Figure 2). The plots fitted to the pseudosecond-order model for both resins were closer to the experimental points than the pseudo-first-order kinetic model. Thus, the kinetics of sorption by both MIEX[®] and AR fit the second-order kinetic model with a reaction rate constant (k_2) of 0.3095 mLmg⁻¹min⁻¹ and 0.0858 mLmg⁻¹min⁻¹, respectively, and a coefficient of determination (R^2) of 0.9972 and 0.9912, respectively. The initial rate constant for MIEX[®] (0.3095 mLmg⁻¹min⁻¹) was much higher than for AR (0.0858 mLmg⁻¹min⁻¹).

Figure 2 Sorption kinetics of 5 mL/L of MIEX® and AR

In addition, the initial sorption rate (h) was 0.2341 mgmL⁻¹min⁻¹ for MIEX[®] and 0.1352 mgmL⁻¹min⁻¹, for AR. These findings imply MIEX[®] is faster in removing DOC than AR. Therefore, designing a sorption system for MIEX[®] would require less contact time and a small reactor than one for AR. This also indicates the pseudo-second-order kinetic model provides a reliable simulation for predicting the sorption of DOC by both resins. The pseudo-second-order model is based on the assumption that chemical sorption is the rate limiting step, involving covalent forces through sharing or exchanging electrons between both resins and DOC [33]. Therefore, the sorption process of DOC on MIEX® and AR is a chemical sorption process. The sorption kinetics of MIEX® and AR of this work were consistent with previous studies [31, 34].

3.2.3 Isotherms

A sorption isotherm explains the relationship at equilibrium between the amount of sorbate adsorbed on the sorbent and the amount of sorbate remaining in the solution. Sorption isotherms are important for sorption systems, as they can be used to quantitatively compare the properties of different sorbents, describe the sorption state of sorbate on sorbent surfaces and calculate sorption parameters such as theoretical sorption capacity. Hence, sorption isotherms usually provide some insight into sorption mechanism and the affinity of sorbent and surface properties. Figure 3 shows a linear equation graph for sorption isotherms of DOC on both resins, following the Langmuir and Freundlich isotherm models. Freundlich models of MIEX® and AR had higher correlation coefficients (0.8869 and 0.6175, respectively) than the Langmuir models (0.5346 and 0.8522, respectively). As such, the sorption of DOC on MIEX® and AR can be modelled using the Freundlich isotherm model, which matches results from other studies [31, 34]. Because of this, sorption of DOC on both resins would not pose any limitations on sorption and would be more proper in situations where the sorption sites are heterogeneous in nature. The Freundlich model is suitable for a highly heterogeneous surface composed of different classes of sorption sites. This model mainly has two assumption: First, an increase in surface coverage of the sorbent leads to a slight decrease in the binding strength and the sorbent energies of active sites on the surface of the sorbent are different. As shown in Figure 3b and 3d, the kF of MIEX[®] and AR were 0.327 mL/mg and 0.226 mL/mg, respectively, while the 1/n values were 3.697 and 2.863, respectively. MIEX[®] had a higher k_F than AR, indicating a larger sorption capacity and higher sorption density. In addition, 1/n is a measure of sorption density and is a heterogeneity factor. That 1/n was over 1 indicates that the sorption of DOC on both resins is favorable because both resins have a large surface area and cooperative sorption.

Figure 3 Sorption isotherms of DOC for (a) the Langmuir isotherm model of MIEX®, (b) the Freundlich isotherm model of MIEX®, (c) the Langmuir isotherm model of AR,and (d) the Freundlich isotherm model of AR

3.3 DOM removal by MIEX@ and AR before coagulation

MIEX[®] and AR were used with and without coagulation (FeCl₃) to investigate the effect of MIEX[®] and AR pre-treatment on subsequent coagulation capabilities (DOC removal and UV $_{254}$) and coagulant demands. Figure 4 presents the effects of MIEX[®] and AR pre-treatment on coagulant effectiveness in DOC removal and UV254. Coagulation/sedimentation by 40 mg/L of FeCl3 alone only decreased DOC by around 2 mg/L. In contrast, pre-treatments by MIEX® or AR decreased DOC from 7.37 to 2.82 and 2.87 mg/L, respectively, which is much better than only coagulation/sedimentation by FeCl3.

Treatments by MIEX® or AR followed by coagulation/sedimentation by FeCl3 (5 mg/L) decreased DOC to below 2 mg/L. Similar changes were observed in UV²⁵⁴ values. These observations on the combined processes were consistent with previous research that used MIEX[®] prior to coagulation; pre-treatment and coagulation removed DOC better than coagulation alone [35]. Moreover, there was a reduction in coagulant demand from MIEX® or AR pre-treatment. Without pre-treatment by ion-exchange resins, optimum demand for FeCl₃ to achieve the lowest DOC values (5.14 mg/L) was 40 mg/L; the optimum demand for coagulants after pre-treatment by MIEX[®] or AR was only 5 mg/L. Thus, MIEX[®] and AR were able to reduce coagulant (FeCl₃) demand by 87.5% during the coagulation process. This is consistent with previous studies on coagulant demand reduction of up to 50%-80% [6].

3.4 Effects of pH on DOC removals

The effects of pH on sorption efficiency for DOC and UV $_{254}$ for both resins was examined using 10 mL/L doses and a 30-minute contact time. The sorption efficiency of DOC and UV²⁵⁴ of MIEX® were 63% and 89% at pH 7, 66% and 89% at pH 8, 63% and 86%

at pH 9. For AR, they were 70% and 91% at pH7, 70% and 91% at pH 8, 69% and 90% at pH 9. These results demonstrate that the effect of initial pH on the sorption of DOC and UV₂₅₄ by MIEX[®] and AR differed slightly for pH values between 7 and 9. As pH from 7-9 were selected from actual characteristics of effluents, both MIEX[®] and AR can be used for effective DOC removal and UV₂₅₄ in SME.

Figure 4 Comparison of DOC removal and UV₂₅₄ for different processes

3.5 Multiple-loading tests

After finding the optimal dose and contact time for both resins, multiple-loading jar tests were conducted to simulate the use of MIEX® and AR in a batch test, as well as the removal capabilities of a continuous ion-exchange process. This determined the number of bed volumes of water sample that both resins could treat before regeneration was necessary. Figure 5 illustrates the results of the multiple-loading jar tests. DOC removal was 62% and 63 % for AR at 200 BV and gradually decreased to 28% and 22%, respectively, at 2500 BV. The percent of DOC remove decreased to 11% for MIEX® and 18% for AR at 4500 BV and remained at this level until 6000 BV. These findings indicate that, after treating 4500 BV equivalents, the removal capacity begins to decrease; the resins occurred saturated between 2500 and 6000 BV, and the saturated resins removed equal amounts of DOC from the water sample between these bed volume loadings. The results from these experiments suggested that both resins could be loaded up to 2500 BV without regeneration. Similar trends were also observed in UV₂₅₄ absorbance reduction (data not shown).

Figure 5 Multiple-loading tests using 5 mL/L of MIEX® and AR

3.6 Molecular DOM removal by MIEX® and AR assessed via non-targeted analysis using Orbitrap mass spectrometry

Recently, non-targeted (or unknown screening) analysis using Orbitrap mass spectrometry has been widely used to investigate changes to molecular DOM in water and wastewater treatment processes [21-38]. This study applied non-targeted analysis to investigate removals of DOM by MIEX® and AR (Figure 6).

Only DOM formulae with carbon, hydrogen, and oxygen atoms (CHO DOM) were considered, as they made up 60% of the formulae found (data not shown). Both resins were similarly selective in decreasing CHO DOM for carbohydrate-like, lignin-like, and condensed aromatic DOM; lipid-like DOM was refractory to both resins (Figures 6a and 6b). For (DBE–O)/C vs C_{os}, both resins were selective in decreasing CHO DOM with relatively oxidized characters (a positive oxidation state; Figures 6c and 6d), while effects on the degree of unsaturation were not obvious. As more oxidized molecules contain more oxygen functional groups (such as OH), resulting in a more acidic character, this makes them prone to adsorption by anion-exchange resins, like those in this study. With this finding, it may be possible to enhance DOM removal by increasing acidity using pre-oxidation before applying anion- exchange resin treatments; this requires further investigation.

Figure 6 Van Krevelen diagram (a, b) and (DBE-O)/C vs C_{os} (c, d) for decreased and refractory CHO DOM. Each plot reveals one molecular formula of CHO DOM through its behaviors during treatment. Decreased CHO-DOM plots (yellow crosses) were formulae that decreased in intensity by over 30% after the treatment; the others (green diamonds) were considered refractory to the treatment.

4. Conclusions

This study investigated the applicability of MIEX[®] GOLD and AMBERLITE™ FPA98 Cl anion-exchange resins for removing DOM from SME. This work demonstrated the following;

The 5 mL/L doses of MIEX[®] and AR achieved removed DOC per unit of resin at 54.82 % after 20 min of equilibrium contact time and 53.93% after 60 min of equilibrium contact time, respectively.

 \bullet The sorption kinetics for DOM in the effluent by MIEX[®] and AR were pseudo-second-order with initial sorption rate constants of 0.31 mlmg⁻¹min⁻¹ and 0.09 mlmg⁻¹min⁻¹, respectively. Sorption isotherms for both resins were fitted with the Freundlich isotherm; the sorption capacity of MIEX® (0.33 mg/mL) was higher than that of AR (0.23 mg/mL). MIEX® had a greater sorption capacity and sorption density than AR. The sorption process of DOC on MIEX[®] and AR is a chemical sorption process. Therefore, designing a sorption system for MIEX® would require less contact time and use smaller reactor than a sorption system for AR.

In multiple-loading tests, DOC removal with MIEX[®] and AR was gradually decreased from 62% to 28% and 63% to 22%, respectively, at 2500 BV. In addition, removal decreased to 11% for MIEX® and 18% for AR at 4500 BV and then remained constant at this level until 6000 BV. DOC removal for both resins occurred between 2500 and 6000 BV. These experiments suggest that both resins could effectively load DOC up to 2500 BV without regeneration in SME.

Pre-treatment with MIEX® or AR before coagulation/sedimentation substantially increased DOC and UV $_{254}$ removal compared to coagulation alone and also reduced FeCl₃ demand by around 87.5%.

 Both resins selectively removed carbohydrate-like, lignin-like, and condensed aromatic DOM; lipid-like molecules with more oxidized characters were not removed by either resin.

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Engineering and Applied Science Research 2022;49(1) 111

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