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# Reduction of Reactor Corrosion by Eliminating Liquid-Phase Existence in Dry Dilute Acid Pretreatment of Corn Stover

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**ABSTRACT:** Serious corrosion of reactor metal walls by aqueous dilute acid solution is one of the essential drawbacks of dilute acid pretreatment (DAP) in the biorefining of lignocellulose biomass. In this study, the corrosion of pretreatment reactor metal walls was significantly reduced by the dry dilute acid pretreatment (DDAP) of corn stover, a modified DAP, in which the aqueous dilute acid solution is completely absorbed by high solids corn stover feedstock. The iron ion release from the stainless-steel walls of the reactor was measured, and the corrosion degree was quantitatively characterized. The reactor corrosion was reduced by approximately 85% when the solid/liquid ratio increased from the conventional value of 1:10 to the high value of 1:0.5 at the same sulfuric acid concentration in the DDAP. The results provided the simple and practical solution to the key technical barrier of DAP and paved the way for large-scale application.

## 1. INTRODUCTION

Dilute acid pretreatment (DAP) is one of the leading pretreatment technologies by effectively dissolving hemicellulose and disrupting the cellulose structure of lignocellulose biomass at low chemical use and operation costs.[1−3] Nevertheless, several essential drawbacks of this method limited its commercial applications. These drawbacks include (1) massive wastewater generation (generally 6−20-fold greater than the solids by weight), (2) high inhibitor compound generation, such as furfural, 5-hydromethylfurfural (HMF), acetic acid, and phenolic aldehydes, and (3) strong corrosion of reactor metal walls by aqueous dilute acid solution.[4,5]

To overcome these drawbacks of this efficient pretreatment method, a modified DAP entitled "dry dilute acid pretreatment (DDAP)" was developed in our previous studies by significantly cutting the freshwater use at the beginning of pretreatment and reducing the hot water steam use during the pretreatment.[4,6] The solid/liquid ratio (the ratio of the dry lignocellulose solids to the aqueous dilute sulfuric acid solution) of the initial feedstock is only 1:0.5 or 67% of the solids content by weight percentage, as compared to the regular solid/liquid ratio of 1:10 (or 10% of the solids content). Then, the hot steam jetting on the lignocellulose feedstock during the pretreatment gives the final solids content of 50% of the pretreated product. This modified method completely eliminates the existence of free dilute acid solution during the whole pretreatment process because all of the water streams, such as fresh acid solutions, hot steam, and wastewater streams, are completely absorbed by the lignocellulose solids. The reduction of wastewater generation by the present DDAP method is achieved by complete removal of wastewater stream in the pretreatment step and reduced freshwater addition in the simultaneous saccharification fermentation (SSF) step at significantly high solids loading up to 30−35% (w/w).[7−9] Therefore, the first drawback of massive wastewater generation is successfully solved.[4,6] The second drawback of high inhibitor generation is solved by introducing the fast and complete biodetoxification by *Amorphotheca resinae* ZN1 fungus on the pretreated lignocellulose solids without any input of freshwater and output of wastewater.[10,11] For the third and final unsolved drawback of reactor corrosion in DAP, the corrosion degree of reactor metal walls should be reduced in the DDAP operation because of the disappearance of aqueous dilute acid solutions inside the pretreatment reactor. In the practical operation, the reduced corrosion phenomenon of the pretreatment reactor metal walls was observed but no quantitative evidence was proposed.

In this study, the reactor corrosion of the pretreatment reactor during the DDAP operation was quantitatively measured by analyzing the iron ion release from the stainless-steel walls of the pretreatment reactors. The result revealed that approximately 85% reduction of the pretreatment reactor corrosion was achieved during the DDAP operation. The results confirm that the DDAP successfully solved the third and final drawback of DAP.

## 2. EXPERIMENTAL SECTION

**2.1. Raw Materials and Reagents.** Corn stover was harvested from Nanyang, Henan, China, in the fall of 2014. Corn stover was washed to remove the field dirts, stones, and metals, then air-dried, and milled using a beater pulverizer to pass through the 10 mm diameter apertures. The milled corn stover was sealed in plastic bags and stored at room temperature until use.

Cellulase enzyme Youtell 6 was purchased from Hunan Youtell Biochemical Co., Yueyang, Hunan, China. The filter paper activity of Youtell 6 was 135 filter paper units (FPU)/g of dry enzyme powder using the National Renewable Energy Laboratory (NREL) LAP-006 protocol;[12] the cellobiase activity was 344 cellobiase units (CBU)/g of dry enzyme powder by the method described by Ghose;[13] and the protein content was 90 mg/g of cellulase determined by the Bradford method.[14]

Sulfuric acid (98%, w/w), formic acid (98%, w/w), and 1,10-phenanthroline monohydrate (99%, w/w) were purchased from

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Table 1. Composition and Cellulose Conversion of the Pretreated Corn Stover under Different Solid/Liquid Ratio and Sulfuric Acid Usage Conditions[a]

| solid/liquid ratio (S/L ratio) | sulfuric acid usage (mg/g of DM) | cellulose conversion (%) | cellulose content (%, w/w) | xylan content (%, w/w) | xylose content (mg/g of DM) | furfural content (mg/g of DM) |
|---|---|---|---|---|---|---|
| 1:10 | 25 | 60.4 ± 6.9 | 51.3 ± 2.6 | 8.4 ± 0.7 | 96.8 ± 2.4 | 12.4 ± 0.4 |
| | 50 | 72.8 ± 0.4 | 51.4 ± 0.6 | 3.7 ± 0.3 | 169.1 ± 7.7 | 18.4 ± 3.4 |
| 1:0.5 | 25 | 59.9 ± 1.8 | 43.6 ± 2.0 | 2.3 ± 0.1 | 13.4 ± 0.4 | 38.6 ± 3.9 |
| | 50 | 40.5 ± 1.0 | 34.1 ± 0.8 | 0.7 ± 0.1 | 9.43 ± 1.9 | 25.8 ± 1.4 |

[a]Corn stover was pretreated for 90 min at 175 °C using 25 and 50 mg/g of DM of sulfuric acid dosages in the tubular reactors. The solid/liquid ratio value (S/L value) of 1:10 represents the value in the conventional DAP, and the S/L value of 1:0.5 represents the value in the DDAP.

Shanghai Lingfeng Chemical Regents, Shanghai, China. Hydrochloric acid (37%, w/w) was purchased from Sinopharm Chemical Regents, Shanghai, China. Methanesulfonic acid (70%, w/w) was provided by BASF, Ludwigshafen, Germany.

**2.2. DAP Operation.** DAP was conducted in the small tubular reactors with the equivalent efficiency to the enlarged reactors.[6] The tubular reactors were made of 304 stainless steel, the most widely used metal material for pretreatment reactors, with 20 mm in inner diameter and 54 mm in length. A total of 1 g of dry corn stover was well-mixed with dilute acid solution and then loaded into the tubular reactors. The reactors were sealed and heated to the required temperature of 175 °C in a muffle furnace and maintained for the required period. Then, the reactors were immediately quenched in an ice bath, and the pretreated corn stover material was discharged and then stored at 4 °C.

The long-term pretreatment assay was conducted for 312 h with 26 successive batch operations. Each batch operation lasted 12 h. The corn stover mixed with dilute acid solution was filled into the reactors directly and run for the next batch operation after the pretreated material was discharged from the last batch. The iron ion containing the liquid portion in the pretreated corn stover material from each batch operation was either directly filtered for the pretreatment operation at a low solid/liquid ratio (1:10 and 1:3) or presoaked with 9.5 mL of ultrapure water and then filtered for the pretreated corn stover material at a high solid/liquid ratio (1:0.5). The obtained liquid fraction from one single pretreatment was used for determination of soluble sugars, inhibitors, and iron concentrations. The solids fraction was dried at room temperature and used for the enzymatic hydrolysis assay and composition determination.

**2.3. Enzymatic Hydrolysis.** Enzymatic hydrolysis of the pretreated corn stover material was carried out according to the NREL LAP-009 protocol.[15] The pretreated corn stover material was washed by 10-fold water, and 0.5 g of the pretreated corn stover material (dry basis) was added to 10 mL of 0.1 M citrate buffer solution (pH 4.8) in a 50 mL flask and then diluted into the solids concentration of 2.5% (w/w). A total of 0.08 mL of cycloheximide (10 mg/mL) was added to avoid the microbial contamination. A total of 20 FPU/g of dry pretreated corn stover matter (DM) of cellulase was added, and the hydrolysis lasted for 72 h at 50 °C in a water-bath shaking incubator.

**2.4. Determination of the Corrosion Degree of Stainless-Steel Walls of Reactors.** The pretreatment reactors were thoroughly washed with 5% (w/w) hydrochloric acid solution and then rinsed with ultrapure water, consequently, to remove the residual metal rusts before pretreatment operation. After the pretreatment, the pretreated corn stover material was diluted to the solid/liquid ratio of 1:10 and then vacuum-filtrated into the liquid and solids fractions. The iron ion concentration in the liquid fraction was determined according to the China Analysis Standard on Heavy Metals and Iron Content (GB 20432.5-2007). Briefly, 0.1 mL of the iron ion containing the liquid sample and 0.1 mL of 10% (w/w) hydroxylamine hydrochloride solution were well-mixed, and then 0.2 mL of 0.15% (w/w) 1,10-phenanthroline monohydrate solution and 0.5 mL of 1 M sodium acetate solution were added. The mixture was diluted to 5 mL and shaken vigorously for 2 min at room temperature. The absorbance of the sample at the wavelength of 508 nm was measured on a Beckman Coulter DU 800 spectrophotometer (Beckman Coulter, Brea, CA, U.S.A.). A total of 0.1 mL of ultrapure water sample was used as the control of zero iron ion concentration.

The corrosion rate of the reactor stainless-steel walls was defined as the losing thickness of the metal pieces in 1 year (365 days) and calculated using the following equation:

$$\text{corrosion rate (mm/year)} = \frac{\Delta g}{S_0 t d} \frac{24 \times 365}{1000}$$

where $\Delta g$ is the weight loss of the metal sample after corrosion (g), which can be converted by iron ion release from stainless-steel walls of the tubular reactors as a result of 67.8% iron content in 304 stainless steel, $S_0$ was the metal surface area contacting the corrosive medium (acid solution in DAP, $m^2$), $t$ was the corrosion time (h), $d$ was metal density ($g/cm^3$), 24 represents 24 h per day, 365 represents 365 days per year, and 1000 is the unit conversion ratio.

**2.5. Analysis of Sugars and Inhibitors.** Cellulose and hemicellulose contents of the corn stover were analyzed using a two-step sulfuric acid hydrolysis method.[16] Glucose, xylose, and furfural were analyzed on high-performance liquid chromatography (HPLC, LC-20AD, RID-10A, Shimadzu, Kyoto, Japan) with a Bio-Rad Aminex HPX-87H column at 65 °C and 0.6 mL/min of 5 mM $H_2SO_4$ as the mobile phase.

## 3. RESULTS AND DISCUSSION

### 3.1. Determination of Equivalent Pretreatment Efficiency in the Small Tubular Reactors.

The conventional DAP with low solids content frequently generates vast dilute acid wastewater stream because of the low solids content and the limited absorption capacity (the solid/liquid ratio of 1:10). The aqueous dilute acid solution contacts with reactor inner walls and leads to the severe corrosion of the metal material. In the modified DDAP, the lignocellulose solids to the dilute acid solution are considerably high at 67% (w/w) (the solid/liquid ratio of 1:0.5) at the start of pretreatment and at 50% (w/w) (the solid/liquid ratio of 1:1) at the end of pretreatment after partial steam is condensed onto the solids. The high solids content results in the completely "dry to dry" process: dry feedstock input and dry product output because all of the dilute acid solution is completely absorbed by the high amount of solids during the whole operation. To accurately evaluate the reactor corrosion between the conventional DAP and the modified DDAP, the pretreatment operations should be conducted at the equivalent pretreatment efficiency in the small tubular reactors. Table 1 shows that the pretreatment under conditions of 175 °C for 90 min with the addition of 25 mg of sulfuric acid/g of solids gave similar cellulose compositions (51.3 and 43.6%) and cellulose conversions (60.4 and 59.9%) at the solid/liquid ratio value of 1:10 for the conventional DAP and 1:0.5 for the modified DDAP, respectively. These pretreatment parameters were used for evaluating the reactor corrosion of the pretreatment experiment.

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The impact of the solid/liquid ratio on the hydrolysis yield and inhibitor generation had been investigated in detail in the previous study. Under the changing solid/liquid ratios, the glucan hydrolysis yield and inhibitor generation are maintained approximately the same, while the xylan hydrolysis yield shows certain reduction as a result of the incomplete conversion at a low moisture level and then completely hydrolyzes in the consequent hydrolysis and fermentation operation. In the present study, the focus is on the corrosion evaluation of the DDAP pretreatment and the small tubular reactors were used to mimic the DDAP operation with a similar pretreatment intensity to that of the DDAP operation in a large-scale reactor. The small reactors were not able to install any mixing apparatus to realize a well mass/heat transfer as in the large reactor.[4] Therefore, the local overdegradation near the reactor wall was inevitably greater and then led to the obvious xylose loss and furfural increase at the higher solids content. The changes in xylose recovery and furfural generation in the small reactors do not reflect the regular DDAP performance or change the erosion yield.

### 3.2. Reducing Reactor Corrosion Degree by DDAP Operation.

The corrosion rate of stainless-steel inner walls of the tubular reactors was used to indicate the corrosion degree by measuring the iron ion release from the stainless-steel walls of the reactors. All iron ions measured in the liquid fraction were bivalent as a result of the excessive addition of hydroxylamine hydrochloride reductant and then selectively reacted with 1,10-phenanthroline monohydrate to format the stable orange compound.

Iron ion release from stainless-steel walls of the tubular reactors during one single pretreatment batch under the same sulfuric acid addition but different solid/liquid ratios was shown in Figure 1. In the two reactors, the same amount of sulfuric acid (25 mg/g of DM) but different solid/liquid ratios (1:10 and 1:0.5) were applied to represent the typical solid/liquid ratios of the conventional DAP and the DDAP. A total of 10 mL of 0.25% (w/w) dilute sulfuric acid in the DAP reactor and 0.5 mL of 5% (w/w) dilute sulfuric acid in the DDAP reactor were added and maintained at 175 °C for 90 min. When the reactors were empty (no corn stover loading), the iron ion release was 0.21 $g/m^2$ in the DAP reactor and 0.15 $g/m^2$ in the DDAP reactor under the same sulfuric acid and different liquid additions. When corn stover was loaded into the reactors, the iron ion release was reduced about half from 0.07 $g/m^2$ in the DAP reactor to 0.03 $g/m^2$ in the DDAP reactor, indicating that the reactor corrosion was reduced under the high solid/liquid ratio with the same sulfuric acid dosage.

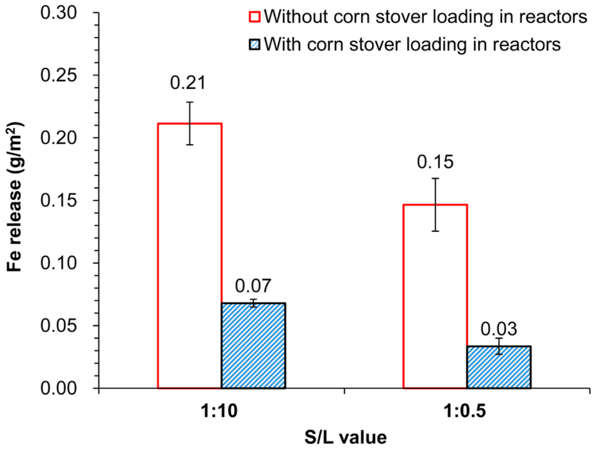

**Figure 1.** Iron ion release from the stainless-steel wall of the tubular reactor after pretreated for 90 min under the same sulfuric acid usage but different solid/liquid ratio values. Conditions: 175 °C and 25 mg/g of DM of sulfuric acid usage. The solid/liquid ratio value (S/L value) of 1:10 represents the value in the conventional DAP, and the S/L value of 1:0.5 represents the value in the DDAP. Experiments were carried out in duplicate.

The accumulative reactor corrosion during the long-term pretreatment operation was shown in Figure 2, which included 26 successive runs of the 12 h batch operations under the same sulfuric acid dosage (25 mg/g of DM). The tendency of reactor corrosion was similar to the single pretreatment operation, in which the iron ion release decreased from 2.03 to 0.98 $g/m^2$ when the solid/liquid ratio increased from 1:10 to 1:0.5. According to the China Standard Method on Metal Corrosion (GB 10124-88), the metal corrosion degree is defined as the losing thickness of metal pieces in 1 year (365 days). Although the corrosion of stainless-steel material includes all of the metal element losses in the stainless steel, the iron ion release from the 304 stainless steel contributed the largest portion of all of the metal losses (67.8% iron content in stainless steel). The losing thicknesses of the tubular reactors calculated by the equation as mentioned in the Experimental Section were 5.13 and 10.60 $\mu$m/year at the solid/liquid ratios of 1:0.5 and 1:10, respectively. According to the classification standards of corrosion resistance, these two values belong to two different levels (levels II and III) of corrosion resistance. The result could be explained by the reduction of the contact surface area with reactor wall material. When acid solution was absorbed quickly by lignocellulose solids under high solid/liquid ratio conditions, no aqueous dilute acid solution led to the reduced reactor wall corrosion.

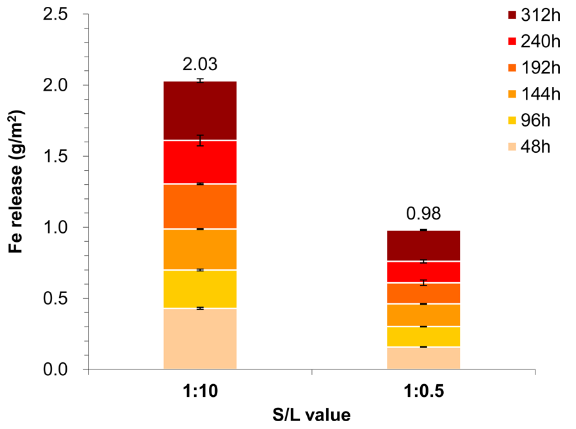

**Figure 2.** Iron ion release accumulation from the stainless-steel wall of the tubular reactor after pretreated for 312 h under the same sulfuric acid usage but different solid/liquid ratio values. Conditions: 175 °C and 25 mg/g of DM of sulfuric acid usage. The S/L value of 1:10 represents the value in the conventional DAP, and the S/L value of 1:0.5 represents the value in the DDAP. Experiments were carried out in duplicate.

The conventional DAP process as described in the technical reports and publications of NREL[17−22] shows the initial corn stover solids content close to 20−45% (w/w) (after impregnation and before pretreatment) and the final solids content close to 30% (w/w) (after pretreatment). Still considerable wastewater is generated by this pretreatment process. In the present DDAP pretreatment method, the initial corn stover solids content is 67% (w/w) (before pretreatment and without impregnation) and the final solids content is 50% (w/w) (after pretreatment). No wastewater stream is generated in the present DDAP.

**3.3. Impact of Operation Parameters on the Corrosion Degree of Pretreatment Reactors.** Several important parameters of pretreatment operations on reactor corrosions were examined, including the solid/liquid ratio, the acid concentration, and the acid catalysis species. Three solid/liquid ratios (1:0.5, 1:10, and 1:3) were chosen to represent the DDAP (1:0.5), the conventional DAP (1:10), and the pretreatment in between (1:3) under the two typical acid concentrations (1 and 5%, w/w). At 1% (w/w) sulfuric acid concentration, the iron ion release was reduced approximately 85% from 1.19 to 0.17 g/m$^2$ when the solid/liquid ratio increased from 1:10 to 1:0.5 (Figure 3a), with the corresponding corrosion rate change from 16.13 to only 2.36 $\mu$m/year. At 5% (w/w) sulfuric acid concentration, a similar tendency of the corrosion rate was observed (Figure 3b). The iron ion release from 1 to 5% (w/w) sulfuric acid concentration at the same solid/liquid ratio increased from 0.17 to 0.39 g/m$^2$, from 0.42 to 0.73 g/m$^2$, and from 1.19 to 2.55 g/m$^2$ at the solid/liquid ratios of 1:0.5, 1:3, and 1:10, respectively. This was easily understood by the aggravated corrosion on the reactor walls with higher acid concentration solution. The results reveal that the high solid/liquid ratio of 1:0.5 significantly reduced the corrosion degree of the tubular reactors.

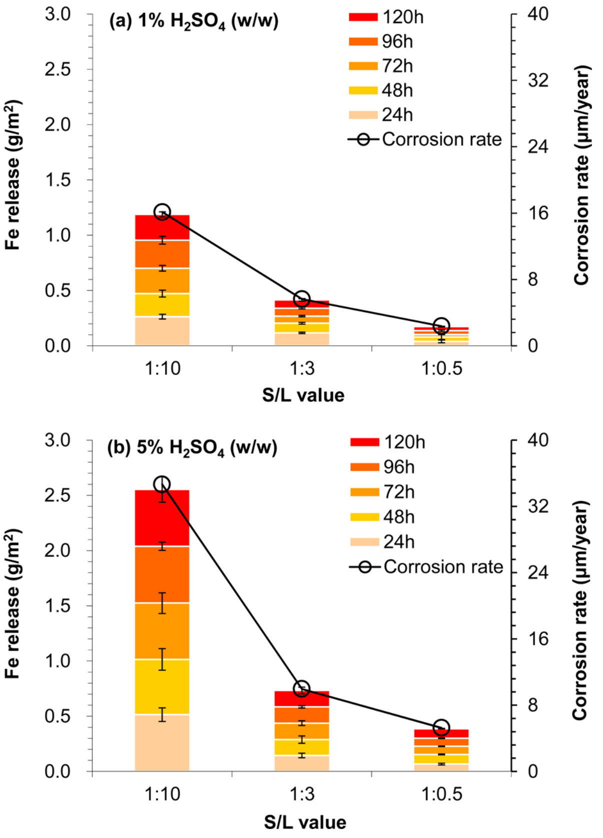

**Figure 3.** Iron ion release from the stainless-steel wall of the tubular reactor under varying sulfuric acid usage and solid/liquid ratio values: (a) 1% (w/w) $H_2SO_4$ and (b) 5% (w/w) $H_2SO_4$. Conditions: 175 °C for 120 h. The S/L value of 1:10 represents the value in the conventional DAP; the S/L value of 1:0.5 represents the value in the DDAP; and the S/L value of 1:3 represents the value in between. Experiments were carried out in duplicate.

Acid species certainly affect the corrosion degree of the pretreatment reactor in DAP. Four typical acids common with the potential use in DAP, including sulfuric, formic, methanesulfonic, and hydrochloric acids, were selected as the catalysts of the DDAP and the conventional DAP operations. For the DAP operation (the solid/liquid ratio of 1:10), the corrosion rate of the tubular reactor using hydrochloric acid was as high as 59.42 $\mu$m/year, 1.7-fold greater than that of sulfuric acid (34.66 $\mu$m/year) (Figure 4a) as well as the other two acids (formic and methanesulfonic acids). For the DDAP operation (the solid/liquid ratio of 1:0.5), the corrosion rate of the tubular reactor was reduced significantly by 78.19, 85.35, 87.16, and 84.82% for hydrochloric, methanesulfonic, formic, and sulfuric acids, respectively (Figure 4b). Clearly, the strong corrosion of hydrochloric acid eliminated the possibility as the catalyst of DAP. Under the same solid/liquid ratio conditions, the corrosion degree by formic, methanesulfonic, and sulfuric acids was similar and the selection of the acid catalyst mainly depends upon the economic consideration. Seemingly, sulfuric acid is on the most proper choice of the acid catalyst list because of the cheap price and availability compared to formic and methanesulfonic acids.

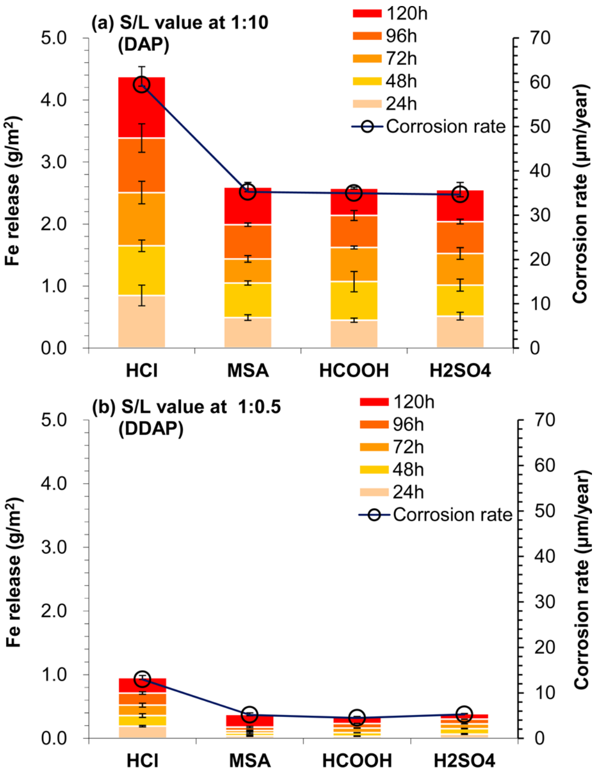

**Figure 4.** Iron ion release from the stainless-steel wall of the tubular reactor using different acids as the catalysts: (a) S/L value of 1:10 representing the value in DAP operation and (b) S/L value of 1:0.5 representing the value in DDAP operation. Conditions: 175 °C and 5% (w/w) acid concentration for 120 h. Experiments were carried out in duplicate. MSA = methanesulfonic acid.

## 4. CONCLUSION

Stainless steel was used as the manufacture material of the pretreatment reactor, and iron ion release from reactor metal walls was measured for the quantitation of the corrosion degree in this study. Pretreatments were conducted under different conditions of the solid/liquid ratio, acid concentration, and acid species. Reactor metal wall corrosion was reduced approximately 85% when the solid/liquid ratio increased from the conventional value of 1:10 to the high value of 1:0.5 at the same sulfuric acid concentration. This study proves that DDAP is a simple and practical method on reduction of reactor corrosion and paves the way for large-scale application.

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### Notes

The authors declare no competing financial interest.

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