

## Leaching characteristics of biomass fly ash in water and a TMP spent liquor: a case study

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### ABSTRACT

Fly ash is considered as an under-utilized product of pulp and paper industry and is mainly land-filled. However, it can be repurposed as an adsorbent for organics of wastewater effluents. Despite efficient adsorption capability, its metal components may dissolve in wastewater and harm the environment. This investigation focused on the leaching behavior of metals from biomass-based fly ash in water at pH 6 and 12.5. A similar investigation was performed in the spent liquor of a pulping process to evaluate the extraction of metals from fly ash in such an environment that fly ash could be used as an adsorbent. The results revealed that the predominant metals leached from fly ash in water and the spent liquor were Ca, K, Mg, Mn, Na, and Si. The trace metals including Al, Ba, Sr, and Zn were also detected to a significant extent. Interestingly, the extraction of metals from fly ash in spent liquor was more limited than in water, which is beneficial for the application of fly ash in spent liquors.

**Keywords:** Fly ash; Metals; Leaching; Lignocelluloses; Thermomechanical pulping; Wastewater

### 1. INTRODUCTION

In a thermomechanical pulping (TMP) process, wood chips are washed and then steamed prior to refining.<sup>1</sup> The effluent that is generated from the TMP pretreatment stage is known as a TMP spent liquor and requires treatments prior to its release into the environment. Adsorption may be a suitable treatment option for pulp and paper mill effluents.<sup>2-4</sup> Gupta and coworkers<sup>5</sup> as well as Wang and Wu<sup>6</sup> have suggested that biomass fly ash may potentially be used as a low-cost adsorbent for treating wastewater effluents. Recently, Oveissi and Fatehi<sup>7</sup> proposed the use of a biomass-based fly ash as an adsorbent for the spent liquor of a TMP process. The results in the previous study suggested that 91.3 % of the COD of a TMP spent liquor might be removed after 2 h of treatment when a biomass fly ash was used at a dosage of 70 mg/g fly ash/TMP with an average particle size of 0.43 mm.<sup>7</sup>

When incinerated, the organic components of fly ash are eliminated, while its inorganic (i.e., metal elements) would remain. These inorganic elements may originate from wood species and/or be introduced to fly ash during the pulping process. The soil properties and wood species type as well as type of pulping process and wood handling practices significantly impact the inorganic elements of wood and thus induced fly ash.<sup>8,9</sup> Regardless of their originality, these elements may be leached from fly ash when left in aqueous systems. Such leaching may introduce an environmental concern for use of fly ash as an adsorbent.<sup>10</sup> Many studies have been performed on leaching metals from coal fly ash.<sup>11</sup> However, relatively few leaching studies have been conducted on biomass fly ash and observations related to

the leaching from coal ash may not apply to that from a biomass fly ash.<sup>12</sup> For example, leaching of Pb from coal does not appear to pose a significant environmental impact,<sup>11</sup> but significant leaching of Pb from biomass fly ash has been observed previously.<sup>12</sup> Since leaching processes are very complex, leaching experiments must be conducted to determine the extent of leaching for a specific system.

Leaching assessment on wood fly ash has been conducted previously. Andersson et al.<sup>13</sup> studied leaching of metals from a wood fly ash in deionized water, and it was determined that the dominant elements in water were K, Ca, S, and Na. In another study by Laohaprapanon et al.,<sup>14</sup> leaching experiment was conducted on a wood fly ash in distilled water at two different liquid-to-solid ratios (L/S) of 5 and 10 at 293 K and for 24 h. The trace metals that were detected to a significant extent in the leachate for the L/S of 5 and 10 were 3.2 and 1.7 mg/L Cr, 0.4 and 0.3 mg/L Zn, 0.3 and 0.4 mg/L Ba, and 0.1 mg/L Pb. Despite valuable information about leaching inorganic materials from fly ash that is generated from wood species in Sweden, these studies are inconclusive to determine the significance of the impact of inorganic metals of fly ash that is generated in northern Ontario. In other words, the results available in literature cannot predict the overall implication of northern Ontario-based fly ash as an adsorbent in treating wastewater produced in the mills located in northern Ontario.

Previous studies indicated that the concentration of a specific metal leached into a system was dependent on its concentration in a fly ash, but no direct correlation on the extent of leaching was observed.<sup>11,12</sup> Furthermore, leaching characteristics of a system appeared to be dependent on a

combination of various factors, such as the type of minerals (e.g., oxides versus sulfides or chlorides), the specific location of the metals (e.g., on the surface versus the interior location), ionic strength of the solution, and the pH of the system.<sup>15</sup> Metals may leach more easily from fly ash samples with a smaller particle size, but the increased surface area may also aid in the adsorption of metals from wastewater on fly ash.<sup>16</sup> To the best of our knowledge, the impact of leaching of a biomass fly ash in a TMP spent liquor was not conducted previously, which was in fact an objective of this paper.

The purpose of this study was to assess the feasibility of using a biomass-based fly ash as an adsorbent with respect to its potential environmental impacts. The main novelty of this paper was the assessment on leaching metals from biomass fly ash in the spent liquor of the TMP process. In this case study, two fly ash fractions with different metal contents were ground to a similar particle size. In this case study, a biomass fly ash was fractionated and ground to yield two fly ash samples with a similar particle size. This exercise was conducted to minimize the potential impact of particle size to provide a means for comparing the impact of their metal contents. Leaching experiments of the two fly ash samples were conducted using two L/S of 100 and 15 at neutral (pH 6) and alkaline (pH 12.5) conditions in both water and in a TMP spent liquor. The results were then evaluated against potential acceptability criteria related to wastewater effluent guidelines of the metal mining sector, since the effluents of the pulp and paper sector are currently not regulated for metal contents.

## 2. EXPERIMENTAL

### 2.1. Materials

Biomass fly ash and a TMP spent liquor were obtained from a pulp mill that is located in northern Ontario, Canada. The fly ash was the residue generated in a boiler that used a mixture of wood and wastewater sludge as fuel. The TMP spent liquor was filtered with a glass filter apparatus (Millipore) and a filter paper (Whatman No. 1), the filtrates were collected and stored in a refrigerator at 277 K prior to any test. The chemical oxygen demand (COD) and lignin of the filtrates were determined as stated in a following section. The fly ash was dried in an oven at 378 K, cooled and then stored in plastic bags at room temperature prior to use. Sodium hydroxide (98 wt. %), hydrochloric acid (37 wt. %), potassium hydroxide and glacial acetic acid (99 wt. %) were purchased from Sigma Aldrich Company. The COD kit (K-7365) was obtained from CHEMetrics Inc., USA.

### 2.2. Fractionation of biomass fly ash

The biomass fly ash was mechanically sieved using ASTM E11 sieves with mesh numbers of 10, 20, and 60

based on the method described previously.<sup>17</sup> In this fractionation step, 200 g of fly ash was sieved at a time using a mechanical sieve shaker (CSC Scientific, Meinzer II Sieve Shaker) and shaken for 10 min. The fly ash that was retained on the sieves with mesh numbers 60 and 20 were collected and denoted as S1 and S2. The fly ash sample was then ground for 20-30 seconds using a grinder (Bel-Art SP Scienceware micro-mill), sieved with mesh numbers of 200 and 400, and the fly ash retained on the sieve number 400 mesh was collected. In other words, the fly ash samples were ground and sieved to the same particle size range to minimize the impact of particle size in the leaching tests.

### 2.3. Leaching tests in deionized water and TMP spent liquor

Biomass fly ash samples were added to 50 g of deionized water or TMP spent liquor in 250 mL Erlenmeyer flasks at a dosage of 10 or 67 mg/g fly ash/water or TMP spent liquor (corresponding to L/S ratio of 100 and 15). These ratios showed promising results in terms of organic removals from TMP spent liquor in our previous work.<sup>18</sup> The pH of the mixture was then adjusted to 6 or 12.5, and the flasks were sealed. The samples were then shaken at 100 rpm in a Boekel water bath shaker at 298 K for 2 h. After the leaching treatments, the samples were filtered with a glass filter apparatus (Millipore) and filter paper (Whatman No. 1). The filtrates were then collected for metal, COD, and lignin analyses. The COD and lignin removals from the TMP spent liquor were determined using equation 1:

$$\text{Removal \%} = \frac{C_0 - C_F}{C_F} \times 100 \quad (1)$$

where  $C_0$  refers to the initial COD or lignin concentrations and  $C_F$  refers to the final COD or lignin concentrations in the filtrates after the leaching/adsorption treatments. All tests were carried out in triplicate and the average results were reported.

Unless indicated otherwise, the background metal contents in the TMP spent liquor were subtracted from the results of the leaching tests of S1 and S2 in a TMP spent liquor in this work. Furthermore, the analysis of the Na that leached into water and the TMP spent liquor by the addition of S2 was omitted, since sodium hydroxide addition for pH adjustment of the solutions interfered with this assessment.

### 2.4. Metal analysis

The metal content of fly ash and leachate samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista Pro with CETAC ASX-510 Auto Sampler. In this method, 0.2 g samples of fly ash were digested with aqua regia (i.e., nitric acid and hydrochloric acid in a 1:3 molar ratio) in a

microwave (CEM Mars Xpress microwave) using an Xpress closed vessel. The digestion conditions consisted of a 20 min ramp time to a temperature of 448 K and 25 min digestion at 448 K. After digestion, the samples were cooled and then diluted with 40 mL deionized water prior to ICP-OES analysis. The leachate samples were analyzed by ICP-OES without pretreatment.

### 2.5. COD, lignin and hemicellulose analysis

The COD analysis was carried out by adding 2 mL samples to COD vials obtained from CHEMetrics. The samples were incubated in a reactor (CR 2200 WTW thermoreactor) for 2 h at 423 K, and their COD was then measured by the spectrophotometric method at 620 nm using a spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific). The lignin analysis was performed based on a spectrophotometric method described previously.<sup>19</sup> The pH of the samples was adjusted to 7 ( $\pm$

0.25) with 0.1 M NaOH or 0.1 M HCl prior to analysis at 205 nm,<sup>20</sup> using a UV-Vis spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific). The concentration of hemicelluloses in the TMP spent liquor was determined using an ion chromatography (Dionex ICS 5000, Thermo Scientific, equipped with an electrochemical detector (ED) and a CarboPac™ SA10 column).

The TMP spent liquor samples were first treated with 4 wt.% sulfuric acid at 121 °C for 1 h in an oil bath to convert oligomeric sugars to monomeric sugars (i.e., dilute acid treatment).<sup>21</sup> The acidulated samples were filtrated by 0.20  $\mu$ m membrane and subjected to the sugar measurement using an ion chromatography (Dionex ICS 5000, Thermo Scientific, equipped with an electrochemical detector (ED) and a CarboPac™ SA10 column). The operating temperature of the column was 303 K, the eluent was 1.00 mM KOH and the eluent flow rate was 1.2 mL/min using an eluent generator (EGC 500 KOH, Thermo Scientific).

**Table 1.** Metal content in two fly ash samples of S1 and S2 and a TMP spent liquor

Metal	S1, mg/kg	S2, mg/kg	TMP spent liquor, mg/L
Al	7894	713	0.14
As	2	<MDL	<MDL
Ba	2277	342	0.16
Be	<MDL	<MDL	<MDL
Ca	177450	29893	18.36
Cd	8	0	<MDL
Co	6	<MDL	<MDL
Cr	10	1	<0.01
Cu	82	9	0.07
Fe	4773	325	0.14
K	36445	8679	23.60
Mg	14774	1605	4.61
Mn	8014	1052	1.15
Mo	<MDL	<MDL	<MDL
Na	6612	1365	14.69
Ni	12	<MDL	<MDL
Pb	17	<MDL	<MDL
Si	1937	1443	3.17
Sr	526	86	0.07
Ti	184	10	<MDL
Tl	<MDL	<MDL	NM
V	9	<MDL	<MDL
Zn	1915	76	0.33

MDL = minimum detection limit

NM = not measured

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of TMP spent liquor and biomass fly ash samples

In Table 1, the metal elements present in S1 and S2 are shown. The results indicate that the total metal content of S1 was 26.3 wt. %, and the major metals present were Ca,

K, Mg, Mn, Al, Na, and Fe. The rest of the metals presented less than 1 wt.% of the total weight and many of them were close or below their detection limits. The results of S2 demonstrated that the total metal content was 4.4 wt. %, where the major elements present were Ca and K. In another study, the main metals detected in a fly ash produced from a kraft pulp mill were 24.8 wt. % Ca, 6.5 wt. % K, 2.2 wt. % Mg, 0.6 wt. % Na, 0.6 wt. % Al, and 0.4 wt.

% Fe.<sup>21</sup> The carbon contents of S1 and S2 were determined to be 23.85 % and 85.01 %, respectively.<sup>18</sup> Sample S2 collected on sieve with mesh number of 20 contained larger particles (0.841-2.00 mm) resulting from the unburned portion of wood chips and branches with high carbon content. More residual incinerated inorganic elements (i.e., salts) were left in sample S1 with smaller particle sizes.

The concentration of the metals detected in the filtered

TMP spent liquor was also provided, and the TMP spent liquor had 2318 mg/L COD, 1.95 g/L lignin, 0.7 g/L hemicelluloses, and pH 6.1. The results in Table 1 indicated that the major metals present in the TMP spent liquor were K, Ca, Na, Mg, Mn, and Si. In another study, it was determined that a TMP spent liquor had 1610 mg/L COD and 4.2 pH, and the concentrations of its main metals were 54.98 mg/L Na, 34.24 mg/L Ca, 33.00 mg/L K, 6.33 mg/L Mg, and 2.32 mg/L Mn.<sup>22</sup>

**Table 2.** Leaching tests of S1 in water under various conditions

L/S	Fly ash treatment			
	pH 6		pH 12.5	
	100	15	100	15
Metal	mg/kg (dry wt.)			
<b>Major metals</b>				
Ca	97580	18749	103750	15793
K	35070	36366	35960	37910
Mg	6635	4739	4	1
Mn	658	339	<MDL	<MDL
Na	5294	5060	5534	5580
Si	1352	468	8	1
<b>Trace metals</b>				
Al	3.70	<MDL	<MDL	<MDL
As	<MDL	<MDL	<MDL	<MDL
Ba	65.00	42.04	48.50	10.86
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	0.39	<MDL	<MDL
Co	1.10	0.50	<MDL	<MDL
Cr	0.20	0.06	0.60	0.29
Cu	0.60	<MDL	<MDL	<MDL
Fe	<MDL	<MDL	<MDL	<MDL
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	0.71	<MDL	0.57
Pb	<MDL	<MDL	<MDL	<MDL
Sr	285.60	162.91	179.10	80.66
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	15.40	1.35	129.10	30.57
<b>Total metal</b>	146960	65929	145613	59407
<b>Total trace metal</b>	372	208	357	123

L/S = L/kg assuming a water density of 1 kg/L

MDL = minimum detection limit

### 3.2. Impact of leaching of fly ash sample (S1 and S2) and concentration

Tables 2 and 3 present the metal components leached from S1 and S2 in water under the conditions of 298 K, 100 rpm, 2 h, with a L/S of 100 or 15 and a pH of 6 or 12.5. The concentration of leached metals as well as percentage of each metal in fly ash leached in water were provided. The L/S ratios was reported to impact the extraction of metals significantly.<sup>18</sup> The pH of 12.5 represents the pH that the treatment of TMP spent liquor with S1 would reach. A leaching time of 2 h was chosen to reflect the potential leaching that may occur via using TMP spent liquor with biomass-based fly ash.<sup>18</sup> The results in Tables 2 and 3 indicated that the main metals that were detected in the filtrates of S1 and S2 were Ca, K, Mg, Mn, Na, and Si; and these results are consistent with the results of leaching studies in water as previously reported.<sup>13</sup> In this study, the

analysis of Na that leached into water by the addition of S2 was omitted, since the leaching at pH 12.5 required the addition of sodium hydroxide, and thus the leaching characteristics of Na from S2 could not be determined in this study.

The findings also showed that as the L/S ratio increased, the concentrations of K and Na did not increase. Metals that were not limited by their solubility in water generally exhibited a detectable concentration in the leachate, which was inversely proportional to the L/S ratio.<sup>23-26</sup> Furthermore, the concentration of leached metals was relatively independent of pH.<sup>26</sup> Thus, the results suggested that the leaching of K and Na appeared to have been based on their availability as their solubility in water is high. However, leaching of Ca-based compounds was pH dependent, as the solubility of these compounds are usually pH dependent in water.

**Table 3.** Leaching tests of S2 in water under various conditions

L/S	Fly ash treatment			
	pH 6		pH 12.5	
Metal	100	15	100	15
	mg/kg (dry wt.)			
<b>Major metals</b>				
Ca	16373	3734	15947	3009
K	7846	7979	7653	7998
Mg	1181	1140	<MDL	<MDL
Mn	599	491	<MDL	<MDL
Na	-	-	-	-
Si	277	181	221	31
<b>Trace metals</b>				
Al	<MDL	<MDL	146.90	52.69
As	<MDL	<MDL	<MDL	<MDL
Ba	105.10	15.35	18.10	6.85
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	0.03	<MDL	<MDL
Co	<MDL	0.09	<MDL	<MDL
Cr	<MDL	<MDL	<MDL	0.08
Cu	<MDL	0.11	<MDL	0.08
Fe	<MDL	<MDL	<MDL	<MDL
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	<MDL	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	48.90	35.29	13.60	8.11
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	4.60	2.76	13.00	1.55
Total metal	26434	13578	24013	11107
Total trace metal	159	54	192	69

The results of the leaching experiments of S1 and S2 in water indicated that metals, such as As and Pb, were not leached to a measurable extent. However, Al, Ba, Cd, Co, Cr, Cu, Sr, and Zn were detected in the leachates of both S1 and S2; and Ni was detected in the leachates from S1.

Furthermore, as the L/S ratio increased, the concentration of Ca, Mg, Mn, Si, Al, Ba, Sr, and Zn increased. Also, the results indicated that the overall amount of the metal extracted from S1 in water was greater than that from S2 in water under similar conditions.

These results were expected since the total metal content in S1 (26.3 wt. %) was significantly higher than that in S2 (4.4 wt. %). However, no correlation was observed for the extent of leaching with respect to the individual metal concentrations present in the samples. For example, the amount of Mn, Ba and Zn that leached from S1 and S2 in water was comparable; although, there was a factor of 7.6, 8.5 and 23.9 times higher concentration of these metals in S1 than S2. The reason for this behavior may be that a greater extent of these metals was located on the surface of S1 and S2.

### 3.3. Impact of leaching of biomass fly ash (S1 and S2) on TMP spent liquor

Tables 4 and 5 present the total amount of metals that leached via treating TMP spent liquor with S1 and S2 under

the same conditions studied in water as described in the previous section. A comparison of the results in Tables 2 and 4 indicated that the total metal content leached from S1 was greater in water than it was in the TMP spent liquor by a factor of 1.1-1.9 for the same leaching conditions. Furthermore, the total trace metal content leached from S1 was greater in water than it was in the TMP spent liquor at pH 6 but contradictory results were obtained at pH 12.5. Also, the total metal content and the total trace metal content leached from S2 was greater in water than it was in the TMP spent liquor by a factor of 1.4-2.7 and 1.5-2.9, respectively, under similar leaching conditions. Therefore, the results demonstrated that the extent of leaching in water was generally more pronounced from S1 and S2 than in the TMP spent liquor.

**Table 4.** Leaching of S1 in TMP spent liquor under various conditions

L/S	Fly ash treatment			
	pH 6		pH 12.5	
Metal	100	15	100	15
	mg/kg (dry wt.)			
Major metals				
Ca	63004	10490	38004	2596
K	35760	38400	33810	37979
Mg	6619	1700	-456	-69
Mn	2877	1040	-63	-17
Na	4091	5495	3902	4879
Si	1283	771	-270	-48
Trace metals				
Al	17.80	20.69	1.90	-2.12
As	1.30	0.57	<MDL	<MDL
Ba	12.80	3.24	167.00	22.36
Be	<MDL	<MDL	<MDL	<MDL
Cd	2.45	0.43	<MDL	<MDL
Co	2.92	1.23	<MDL	<MDL
Cr	-0.20	-0.03	-0.20	0.21
Cu	3.90	0.47	-5.40	-0.90
Fe	-10.25	-1.87	-14.25	-2.14
Mo	<MDL	0.74	<MDL	<MDL
Ni	4.41	1.38	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	201.55	40.38	91.15	69.74
Ti	<MDL	<MDL	<MDL	<MDL
V	1.10	0.63	<MDL	<MDL
Zn	309.60	58.35	-0.90	25.90
Total metal	114182	58022	75166	45433
Total trace metal	547	126	239	113

L/S = L/kg assuming a water density of 1 kg/L

MDL = minimum detection limit

**Table 5.** Leaching of S2 in TMP spent liquor under various conditions

L/S	Fly ash treatment			
	pH 6		pH 12.5	
Metal	100	15	100	15
	mg/kg (dry wt.)			
Major metals				
Ca	6924	2066	704	352
K	5286	5826	8060	6112
Mg	720	1019	-244	-64
Mn	284	451	32	-4
Na	-	-	-	-
Si	360	269	194	16
Trace metals				
Al	6.57	3.75	111.05	48.91
As	<MDL	<MDL	<MDL	<MDL
Ba	89.40	11.96	-4.85	1.13
Be	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	<MDL	<MDL	<MDL
Co	<MDL	<MDL	<MDL	<MDL
Cr	-0.20	-0.03	0.05	0.01
Cu	1.23	0.52	2.80	-0.24
Fe	1.42	0.87	4.55	-1.25
Mo	<MDL	<MDL	<MDL	<MDL
Ni	<MDL	<MDL	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL
Sr	-6.85	-0.98	4.05	2.95
Ti	<MDL	<MDL	<MDL	<MDL
V	<MDL	<MDL	<MDL	<MDL
Zn	1.93	2.09	-18.55	-4.49
Total metal	13668	9649	8845	6459
Total trace metal	94	18	99	47

L/S = L/kg assuming a water density of 1 kg/L

MDL = minimum detection limit

The metals that appeared to leach to a significantly lower degree in the TMP spent liquor than in water under all conditions studied were Ca, Mg, Sr from S1; S2, Fe, Cr from S1; Ba and Zn from S2. The results given in Tables 4 and 5 also indicated that the concentration of several of these metals were lower than that of the original TMP spent liquor. Thus, the metals that were originally present in the TMP spent liquor may have been adsorbed onto S1 in the adsorption treatment of the TMP spent liquor. According to the literature, wood fly ash could act as an adsorbent for metals.<sup>27-31</sup> However, the leaching of metals such as Al, As, Cd, Co, Cu, Ni, V, and Zn from S1 and Si, Al, Cu, and Fe from S2 was increased at pH 6 in the TMP spent liquor when compared with that in water.

The decreased leaching of S1 and S2 in the TMP spent liquor, when compared with that in water, may stem from the presence of lignin and hemicelluloses in the TMP spent liquor. Previous studies indicated that lignin had an affinity for metal ions and may be used as an adsorbent for metals.<sup>32-35</sup> In other studies, it was reported that dissolved organic matter had an affinity for adsorbing metal ions.<sup>36-38</sup> The main mechanism of metal ion adsorption on lignin appeared to be attributed to electrostatic interactions with

deprotonated hydroxyl phenolic groups and carboxylic acid groups on lignin.<sup>32</sup> Since hemicelluloses contain carboxylic acid groups, it was hypothesized that the adsorption of metals may also have also occurred on the hemicelluloses present in the TMP spent liquor. Furthermore, the complexation of lignin with metal ions was reported to occur within 20 min.<sup>32</sup> Since all of the leaching tests were conducted for 2 h, it was expected that there was sufficient time for the adsorption of metal on lignin to occur in this study. Thus, the reduced leaching observed from S1 and S2 in the TMP spent liquor may be due to the adsorption of the dissolved metals onto lignin and hemicelluloses on fly ash.

Another possible explanation of the decreased leaching of the metal in the TMP spent liquor may originate from precipitation. Previous studies showed that the interaction of lignin with other dissolved organic matter increased the solubility and mobility of metals present in solutions.<sup>37-39</sup> However, other studies observed that the complexation of metals ions on dissolved organic matter could form precipitates and thus the presence of dissolved organic matter might decrease the solubility and mobility of various metals.<sup>40-42</sup> Therefore, lignin and hemicelluloses may have

formed complexes in the presence of some metals in this study. Accordingly, the observed decreased leaching of metals from S1 and S2 in the TMP spent liquor may have been due to the subsequent removal of lignin-metal and hemicellulose-metal complexes from the solution in the filtration step of fly ash from treated spent liquor. These hypotheses can be supported by the reduced lignin and hemicellulose contents after adding fly ash. In this study, after adding fly ash at an L/S of 100 L/kg, the residual lignin and hemicellulose contents in TMP spent liquor were 0.96 - 1.30 and 0.22 - 0.73 g/L, respectively. As expected, at a lower L/S of 15 L/kg, the residual lignin (0.10 - 0.37 g/L) and hemicellulose (0.16 - 0.53 g/L) contents were even lower.

### 3.4. Impact of pH on leaching from S1 and S2 in water and TMP spent liquor

The leaching results from S1 (Table 2) illustrated that pH did not have a significant impact on the total amounts of metals and trace metals that leached into water when the

L/S was 100. The reason for this behavior may be the fact that the maximum possible leaching was made at this ratio and the process conditions could not increase the leaching. However, when the L/S was 15, the total metal and the trace metal contents leached from S1 into water were significantly higher at a pH of 6 than pH 12.5. The leaching results of S2 (Table 4) indicated that the total metal content that leached into water was pH dependent. The reason for this behavior may be the fact that the metals had partial dissolution in water and thus pH facilitated their dissolution.

The leaching results from S1 and S2 in the TMP spent liquor (Table 5 and 6, respectively) demonstrated that pH had a significant impact on the leaching of total metal and trace metal. In this case, the leaching was more pronounced at pH 6 than at pH 12.5. Interestingly, although the magnitude of leaching in water and TMP spent liquor differed, the leaching trends observed with respect to pH were similar for S1 and S2.

**Table 6.** Comparison of the leachates of S1 and S2 in TMP spent liquor with acceptability criteria of the metal mining sector

Metal	Fly ash treatment				Daily limit <sup>a</sup> , mg/L	Monthly average limit <sup>a</sup> , mg/L
	pH 6		pH 12.5			
	100 L/S	15 L/S	100 L/S	15 L/S		
mg/L						
S1 in TMP						
As	0.01	0.04	<MDL	<MDL	1.0	0.5
Cu	0.11	0.10	0.01	0.01	0.6	0.3
Ni	0.04	0.09	<MDL	<MDL	1.0	0.5
Pb	<MDL	<MDL	<MDL	<MDL	0.4	0.2
Zn	3.43	4.22	0.33	2.06	1.0	0.5
Removal, %						
COD	47.1	90.1	46.3	89.2		
Lignin	50.8	94.7	38.2	85.1		
Metal	Fly ash treatment				Daily limit <sup>a</sup> , mg/L	Monthly average limit <sup>a</sup> , mg/L
	pH 6		pH 12.5			
	100 L/S	15 L/S	100 L/S	15 L/S		
mg/L						
S2 in TMP						
As	<MDL	<MDL	<MDL	<MDL	1.0	0.5
Cu	0.08	0.10	0.08	0.11	0.6	0.3
Ni	<MDL	<MDL	<MDL	<MDL	1.0	0.5
Pb	<MDL	<MDL	<MDL	<MDL	0.4	0.2
Zn	0.35	0.48	0.14	0.15	1.0	0.5
Removal, %						
COD	30.8	71.9	29.7	72.2		
Lignin	43.5	89.1	33.2	81.0		

L/S as L/kg assuming a water density of 1 kg/L

MDL = minimum detection limit

<sup>a</sup> Environmental Protection Act, 1990, O. Reg. 560/94<sup>44</sup>



### 3.5. Potential environmental impact of using S1 and S2 on a TMP spent liquor

Table 6 shows the concentrations of various potentially environmentally significant metals detected in the filtrates after the addition of S1 and S2 in TMP spent liquor as collected (i.e., TMP spent liquor background levels were not subtracted). The COD and lignin removals were observed and the daily and monthly average concentration limits for the metal mining sector were given. An assessment of the results indicated that all criteria would be met for the use of S1 as an adsorbent under the conditions of 10 mg/g fly ash/TMP spent liquor, pH of 12.5, 100 rpm and 2 h, where 46 % of COD and 38.2 % of

lignin could be removed, which was optimum for the removal of lignocelluloses from TMP spent liquor by treating it with fly ash. An evaluation of the results for S2 in TMP spent liquor demonstrated that all acceptability criteria would be met for the use of S2 as an adsorbent for all conditions tested. Furthermore, the results showed that 72.2 % of COD and 81.0 % of lignin could be removed under the conditions of 67 mg/g fly ash/TMP spent liquor, pH of 12.5, 100 rpm and 2 h. However, the environmental impact of using S1 or S2 as an adsorbent in a TMP spent liquor with respect to the potential leaching of other regulated chemical parameters such as mercury and polycyclic aromatic hydrocarbons (PAHs) are unknown.<sup>43</sup>

## 4. CONCLUSIONS

A biomass fly ash from a TMP mill was analyzed for leaching its metal elements in water and TMP spent liquor. The results confirmed that the ash could be safe for landfill disposal in Ontario. The major metals that were detected in the filtrates were Ca, K, Mg, Mn, Na, and Si, the trace metals that were detected to a significant extent were Al, Ba, Sr, and Zn, where the concentration of the remaining metals, such as As, Cd, and Cr, were 0.2 mg/L or lower than the tested limits. Under the experimental conditions, the extent of leaching from biomass fly ash was significantly different in water than in the TMP spent liquor, and it was greater in water. The pH of experiment marginally affected the leaching of metals in water, but pH influenced the extraction of metals in the spent liquors. Due to their reasonable extraction, the leaching of metals did not pass the maximum allowable concentration of metals in wastewater. The leaching behavior of metal elements from fly ash could be used as a reference for feasibility assessment in other studies for varied applications of biomass fly ash.

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