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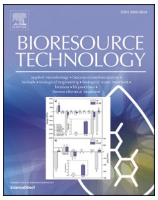

Step washing: A modified pretreatment approach for industrial applications to improve chemical composition of agricultural residues

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HIGHLIGHTS

- A novel pretreatment approach was tested to improve fuel composition of biomass.
- Lab- and pilot-scale testing was done for the novel washing pretreatment.
- Upto 99% Cl, 92% K, 80% S, 72% ash, and 60% N removal was achieved by step-washing.
- Much lower fouling, slagging and corrosion propensity was found after step-washing.
- Pressing and high-water temperature further increase washing efficiency by 6–24%.

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ABSTRACT

To improve the efficiency and applicability of the washing pre-treatment for combustion, pyrolysis and gasification, a modified approach was developed in the present study. Two novel washing approaches were tested using wheat straw and empty fruit bunches of oil palm: multiple-step washing with fresh water (SWFW) and wastewater recirculation (SWWR). SWFW showed the high removal of K (<68%), Cl (<99%), S (<80%), N (<58%), and ash (<52%) reducing fouling, slagging, and corrosion propensity of the biomass. Furthermore, with one-third the amount of water used in SWFW, SWWR showed similar to higher efficiency than SWFW with relatively better energy (98%) yields. Industrial-scale pilot testing was also conducted for the validation of the SWWR approach, which showed similar findings as the lab-scale results. The effect of a high washing temperature and pressing on washing efficiency and characterisation of wastewater was also determined. Overall, SWWR with pressing is recommended for industrial applications.

1. Introduction

Among the various types of biomasses, residues from short-term rotation crops (wheat straw, rice straw, cotton stalk, miscanthus, etc.) and industrial processing (olive residues, empty fruit bunches, bagasse, etc.) are specially generated in large amounts. Wheat is one of the most cultivated cereal crops globally, and annually about 600 million tonnes of wheat straw (WS) is generated worldwide (Bakker et al., 2013). Palm oil production is a huge industry in countries like Indonesia, Malaysia, Thailand, and Colombia which altogether generates around 50 million tonnes of empty fruit bunches (EFB) annually as a by-product (Anyaoha et al., 2018). Due to their ample quantity and availability, there is a high incentive to utilise WS and EFB in different thermochemical processes for energy and product recovery. However, their elemental composition often limits their valorisation in different thermochemical processes such as combustion, gasification, and pyrolysis.

Short-term rotation crops and fruits can quickly take up a substantial amount of nutrients from the soil, such as nitrogen (N), sulphur (S), potassium (K), phosphorous (P), calcium (Ca), magnesium (Mg), and iron (Fe) (Vassilev et al., 2010). The higher content of these nutrients, specially alkali metals and chlorine (Cl), are the root cause of major problems in different thermochemical processes. Cl and S present in the biomass acts as a shuttle in the reactions during combustion, facilitating the transfer of alkali metals into the gaseous form (Hupa et al., 2017; Niu

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et al., 2016). These alkali chlorides and sulphates lead to severe problems in combustion and gasification, such as corrosion, fouling, slagging, higher particulate matter emission, lower ash fusion temperatures, etc. (Jenkins et al., 1996; Morris et al., 2018; Niu et al., 2016). Agricultural residues often contain high amounts of N (<3.4%) and S (<1.1 %), which results in elevated NO_x and SO_x emissions during combustion, contributing to global warming and environmental pollution (Vassilev et al., 2010). In combustion, Si, Ca, Mg, and P in biomass often react with alkali metals to form low melting eutectics (500–800 °C) responsible for intense agglomeration (Hupa et al., 2017; Vassilev and Vassileva, 2019). To mitigate the above-mentioned technical and environmental challenges, pre-treatment of the agricultural residues is essential.

The benefits that make water-washing pre-treatment more attractive for industrial applications are its operational simplicity, high efficiency for removing alkali elements, low cost, and lower energy losses. After washing, higher heating values (0–17% increment) (Deng et al., 2013; Singhal et al., 2021b; Singhal et al., 2021c), ash-melting temperatures (up to 300–500 °C) (Jenkins et al., 1998) and lower ash content (24–80% removal) (Deng et al., 2013; Wu et al., 2019) can be expected, due to which net combustion performance of the feedstock improves considerably. Washing also results in better bio-oil yields in pyrolysis (Cen et al., 2019; Tan et al., 2018) and syngas yields in gasification, with fewer deposition-related issues (Link et al., 2012). High removal of K (38–85%), Na (43–100%), S (20–75%), Cl (28–100%), and ash (5–73%) from WS and EFB was found in past washing studies (Lam et al., 2014; Ma et al., 2017; Singhal et al., 2021c; Tan et al., 2018). Fewer studies reported the removal of N (4–46%), Si (0–65%), P (10–43%), and Ca (2–24%) from WS and EFB (Singhal et al., 2021c; Tan et al., 2018).

To exploit the benefits of washing pre-treatment, researchers have tried to improve its efficiency by altering the basic washing parameters. Singhal et al. (2021b) found a higher removal of problematic elements (K, Na, Cl, S, N, P) for WS on increasing the washing time. For EFB, continuous removal of ash and K was observed on increasing washing duration (Lam et al., 2014; Singhal et al., 2021a; Tan et al., 2018), though the removal of other problematic elements is yet to be determined. Deng et al. (2013), and Lam et al. (2014) found that higher washing temperatures increase the removal of problematic elements by up to 20%. Though the washing pre-treatment is a simple and effective method, further modifications are still required for industrial-scale implementation. Most washing studies utilised a high S:L ratio (>1:20), high temperatures (50-90℃), longer washing durations (3–24 h), and smaller feedstock size (<1cm), making industrial-scale washing unfeasible due to the higher capital and operational costs, and greater operational complexity (Singhal et al., 2021b; Singhal et al., 2021c). For that reason, smaller washing durations (<30 min) and larger feedstock sizes (>1 cm) are more favorable for large-scale operations. Singhal et al. (2021a) and Bandara et al. (2020) found some improvement in biomass fuel properties at smaller washing durations but the removal efficiencies of the problematic elements in these cases were insufficient. Though above-mentioned washing studies have contributed significantly to the improvement of the washing method, the optimal method for industrial-scale washing is still yet to be determined. No studies were found which have focused on industrial-scale washing or the modification of washing process for practical application. Furthermore, no pilot-scale washing studies were found in the available body of knowledge to validate the effect of washing on a larger scale. Due to these limitations, there is a high motivation to develop a modified washing approach focusing on practical applications.

One important issue that directly affects the feasibility of the washing pre-treatment and still remains unaddressed is the handling of effluent wastewater. Currently, detailed wastewater characterisation is missing from the available literature. Deng et al. (2013) and Jenkins et al. (2003) have suggested washing leachate for irrigation purposes due to the high content of K, N, and P. However, the detailed characterisation of washing wastewater is essential for its valorisation, as some heavy metals may leach in considerable amounts during washing (Vassilev et al., 2012; Vassilev and Vassileva, 2019). Mechanical pressing can be used for further removal of troubling elements and absorbed water from the washed biomass. However, its precise effect is yet to be determine.

In the present study, by washing biomass in multiple steps, the washing pre-treatment was modified for industrial applications using counter-current leaching approach. A novel test method was designed to perform a batch washing pre-treatment in multiple steps with and without wastewater recirculation. WS and EFB were selected for the present study due to their huge annual production and availability. First, a total of 28 step-washing laboratory experiments were carried out for 4–30 min. Two experiments (at 20 °C and 40 °C) were performed with wastewater recirculation for each feedstock to reduce water consumption. Pilot testing was also performed with mechanical pressing to test the performance on a larger scale. Also, washing wastewater was characterised to evaluate the potential treatment options.

2. Materials and methods

2.1. Sample preparation and laboratory washing experiments

The WS used for the experimental studies was collected in August 2020 from Lempäälä, Finland. For the pilot testing, WS was collected in bulk from Jyväskylä, Finland. The EFB used in the study was transported from Malaysia to Tampere, Finland. As the moisture content in the WS was ~5%, all the washing experiments were done on as-received basis, while the EFB samples (~51% moisture) were dried and then used after putting them in an open environment for 24 h. For all the washing experiments, 7 g of the sample and 105 ml of water were used (1:15 S:L ratio). Temperature-controlled conditions were maintained for all the washing experiments with mixing at 100 rpm. 3 cm (±0.3 cm) size was used for WS and 3–4 cm (±0.5 cm) size was used for EFB, both were achieved by using scissors. As-received WS and EFB were shredded to 3–5 cm using a branch shredder for pilot testing.

Three types of washing experiments were conducted in the present study: single-step washing with fresh water and multiple-step washing with fresh water (SWFW) and with wastewater recirculation (SWWR). A total of 11 laboratory washing experiments were conducted for each feedstock, of which two were SWWR (Table 1). The procedure for all the step-washing experiments is shown in Fig. 1. To replicate the three-step SWWR scenario, at least three experiments were required to start the process, and the fourth experiment was the actual SWWR. In the present study, two extra experiments (i.e. a total of 6 experiments for each

Table 1
Experimental test matrix for washing experiments conducted in the present study.

	Washing type	Washing steps	Washing duration in each step (*x*)	Washing temperature
Laboratory-scale testing	With fresh water (SWFW)	Single step (*x min)*	2 min	20 °C
			5 min	20 °C
			10 min	20 °C
		Two steps (*x* + *x* min*)*	2 min	20 °C
			5 min	20 °C
			10 min	20 °C
		Three steps (*x* + *x* + *x* min*)*	2 min	20 °C
			5 min	20 °C
			10 min	20 °C
	With wastewater recirculation (SWWR)	Three steps (*x* + *x* + *x* min*)*	5 min	20 °C
			5 min	40 °C
Pilot-scale testing	With fresh water (SWFW)	Single steps (*x min)*	10 min	25 °C
	With wastewater recirculation (SWWR)	Two steps (*x* + *x* min*)*	5 min	25 °C
			5 min	45 °C

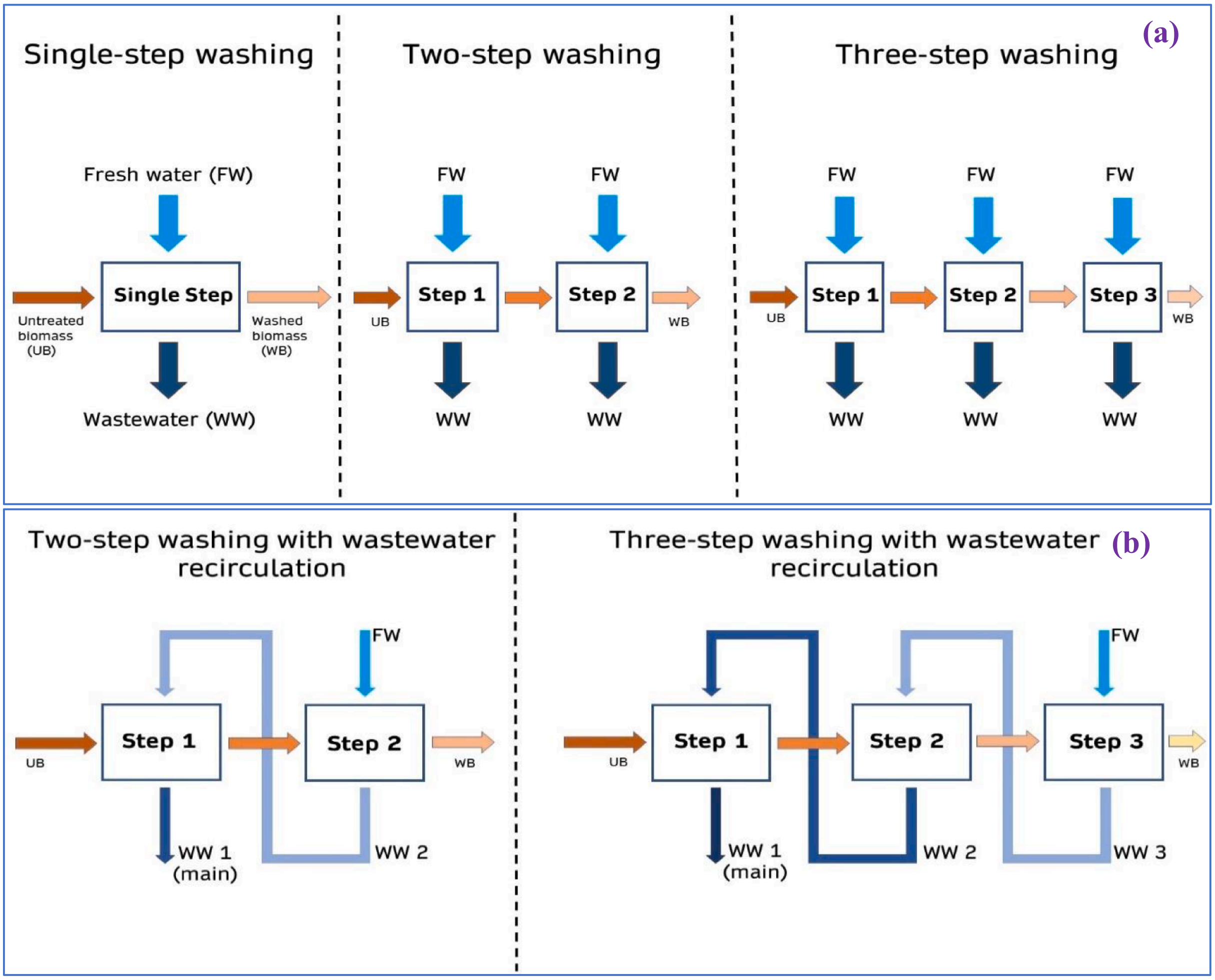

Fig. 1. Schematic of the single- and multiple-step washing experiments (a) with fresh water only (SWFW) and (b) with wastewater recirculation (SWWR).

SWWR experiment) were done to assess the relatability of the SWWR after the fourth experiment. After the third experiment, the system shows consistent results, demonstrating the high reliability of the SWWR approach (more information and validation provided in supplementary material). The results of the sixth experiment were considered as actual SWWR case results and used in the study for all data analyses and comparisons. Before utilising the wastewater for recycling, it was quickly analysed for electrical conductivity (EC), pH, K^+, and Na^+ content. After treatment and leachate separation, all the biomass samples were dried overnight at 103 ± 2 °C and then left in an open environment (maintained at 22 °C) for 24 h (Deng et al., 2013). After that, the samples were preserved in tightly closed boxes and used for further analysis. Parallel to the washing studies, error analysis was also performed which is shown in detail in supplementary material. Single-, two- and three-step washing experiments with each washing step time of 5 min was repeated thrice (total 9 replication) for error analysis. While for EFB, three-step washing experiment with 5 min of washing provided in each step was repeated thrice for calculating error. As per the error analysis results of washing approach, maximum possible error found in the removal efficiencies was<3%. That means all the washing approaches showed in the present study has very small variability and all the results show in the present study are reliable. The step-washed samples are represented as "$x + x + x$", where × is the washing duration of the step and the number of times × is used represents the number of washing steps performed.

2.2. *Pilot testing, effect of pressing, and wastewater production*

To check the effect of upscaling the SWWR, pilot testing was done at the Valmet R&D centre in Tampere, Finland. Two-step SWWR was selected for the pilot testing of WS and EFB as it is more favorable for practical applications and shows a similar efficiency as three-step washing. A rotary drum reactor (Diameter: 1.50 m; Width: 34 cm; pilot washing apparatus shown in supplementary material) was used for washing 11 kg of EFB and 7 kg of WS (S:L ratio 1:20) in each experiment with 30 rpm rotation. Three experiments were conducted with each feedstock (Table 1). SWWR pilot tests were conducted in three phases to replicate the two-step SWWR (shown in Fig. 1). In the first phase, wastewater was generated by washing a batch of fresh feedstock with fresh water. In the second phase, this wastewater was used to wash a fresh batch of biomass (step 1 of two-step washing). In the third step, this used leachate was removed from the reactor and the reaming feedstock was washed again with fresh water (step 2). Part of the wastewater from steps 1 and 2 was collected separately and sent for characterisation. All the washed feedstock samples were stored in a metal cart after washing. Three samples were collected randomly from the cart for each experiment from different depths and sent for drying and further analysis. To evaluate the effect of pressing on the fuel quality of washed feedstock, part of the sample from 5 + 5 min washed at 45 °C was collected separately. This sample was pressed and dewatered using a Saalasti press (Equipment: SP1615S). Biomass was dewatered between a declined perforated drum and a heavy press roll revolving within the drum with the same peripheral speed. During several rotations, effluent flows out through the holes in the drum leaving behind a dry homogeneous material. After pressing, the sample and leachate resulted from the pressing, and both were collected separately and kept for further analysis. Wastewater resulting from step 1, step 2, and the pressing of WS was further characterisation.

2.3. Analytical methods used for evaluating biomass composition and wastewater characterisation

After washing and drying, all the samples were analysed for proximate, ultimate, high heating value (HHV), and elemental composition. The air-drying method was used for determining moisture content (MC) in the feedstock by using an oven at 104 ± 2 °C. Ash and volatile content (VS) of the biomass were determined using standard methods ASTM E1755 – 01 (2007) and ASTM E872 – 82 (2006), respectively. Fixed carbon content was calculated by deducting the MC, VS, and ash from the total content. An elemental analyser (Thermo Scientific™ Flash Smart™ Elemental Analyzer) was used to determine CHNS content of the biomass as per BS EN 15104:2011. O content was calculated by the difference. S content in both the feedstock was found very small to be detected by the elemental analyser. So, for calculating the S removal after washing, S content in the ash was used. X-ray fluorescence (XRF) method (Thermo Scientific™ Niton XL3t GOLDD +) was used to determine the elemental composition of the ash as per ASTM D4326. The analytical methods are further explained in-detail in Singhal et al., 2021b. All the samples were analysed in triplicate for proximate, ultimate, and HHV analysis. HHVs were calculated using the proximate and ultimate composition data, using the relation determined in (Channiwala and Parikh, 2002):

$$HHV\ (MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \tag{1}$$

Where C, H, S, O, N, and A are carbon, hydrogen, sulphur, oxygen, nitrogen, and ash content in the biomass, respectively (wt% on dry basis).

Mass and energy yield of all washing cases were calculated by using:

$$\text{Massyield} = \left(\frac{m_w}{m_o}\right) \times 100\% \tag{2}$$

$$\text{Energyyield} = \left(\frac{HHV'_{ar,mf} \times m_w}{HHV_{ar,mf} \times m_o}\right) \times 100\% \tag{3}$$

where m_w and m_o are the sample's weight before and after washing, and $HHV'_{ar,mf}$ and $HHV_{ar,mf}$ are the HHV of the original and washed samples (as-received and moisture-free basis).

The relation provided by (Deng et al., 2013) was used for calculating the removal efficiency of various elements:

$$\text{R}x = \left(1 - \frac{m_w \times R_w}{m_o \times R_o}\right) \times 100\%,$$

where R is the removal efficiency, x is the removed element, and R_o *and* R_w are the mass fractions of the respective elements in the original and washed samples, respectively.

Washed feedstock samples collected from the pilot testing and pressing were sent for analysis to Eurofins testing laboratory at Kotka, Finland. After drying, the samples were analysed for proximate, ultimate, and HHV using the same methods as above before. To determine the K, Na, and P content, samples were digested with HNO_3 and HF in a controlled microwave oven (CEM Corporation MARS 6) and analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Thermo ScientificTM iCAPTM RQ at TAU, Finland). Leachate collected from each of the laboratory washing experiments was filtered through 0.45 μm filter and analysed for EC, pH, K^+, and Na^+ content using LAQUAtwin K^+ and Na^+ meter and Ion chromatography (Dionex ICS-2100). Wastewater samples collected from the pilot testing were filtered and characterised for various parameters such as COD (as per ISO 15705:2002), BOD (SFS-EN 1899–1:1998), total nitrogen (SFS 5505:Modified Kjeldahl method with Ion chromatography), troubling elements concentration (K, Na, Cl, P), and ions (Cl^- and NH_4^+) (using ICP-MS and Ion chromatography).

2.4. Indexes used for fouling, corrosion, and slagging prediction

In the present study, four empirical relations were used to predict fouling, corrosion, and slagging in the boilers: alkali index (Garcia-Maraver et al., 2017), base-to-acid ratio (B/A) (Gudka et al., 2016), chlorine content (wt% in biomass) (Garcia-Maraver et al., 2017) and slagging index (S_i) (Gudka et al., 2016). The formula for the indexes is:

$$Alkali\ index(AI) = F_{ash}(F_{K2O} + F_{Na2O})/HHV \tag{4}$$

Here F_{ash} is the mass fraction of ash in feedstock (on dry-basis), HHV expressed in GJ/kg, and F_{K2O} and F_{Na2O} is the mass fraction of K_2O and Na_2O in ash. AI < 0.17 means probable fouling, while AI > 0.34 means fouling is certain to occur (Gudka et al., 2016).

$$\text{B/A} = \frac{K_2O + Na_2O + CaO + MgO + Fe_2O_5 + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2} \tag{5}$$

For B/A, < 0.5, very low fouling risk; 0.5 ≤ B/A ≤ 1 medium fouling risk; and B/A > 1 means fouling will definitely occur (Garcia-Maraver et al., 2017).

For Cl (%) in biomass, >0.5 extremely high slagging risk; between 0.3 and 0.5 means high slagging risk; 0.2–0.3 means medium slagging risk; and < 0.2 means low slagging risk (Garcia-Maraver et al., 2017).

$$\text{Si} = \frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \times 100 \tag{6}$$

For $S_i < 66$, extremely high slagging risk; $66 \le S_i \le 78$, medium slagging propensity; and $S_i > 78$, very low slagging propensity (Gudka et al., 2016).

3. Results and discussion

3.1. Effect of step washing using only fresh water (SWFW)

3.1.1. General effect of washing and impact on ash removal

As elemental composition and fuel properties are the main parameters when selecting biofuels for thermochemical conversion, they were analysed thoroughly in the present study. From Tables 2 and 3 and Figs. 2 and 3, it was evident that the washing pre-treatment has a high impact on the composition of both the feedstocks. At short washing durations (2–5 min), a rapid and much higher improvement in the composition (proximate, ultimate, and elemental) was seen for EFB compared to WS. A continuous increment in the volatiles and reduction in ash content can be seen for both the feedstocks on increasing the washing steps. The highest ash removal was seen in the sample 5 + 5 + 5 min (27% for WS and 53% for EFB). The reason behind this high reduction in ash content was the removal of extraneous species (dirt, sand, grit) and the leaching of water-soluble inorganic species (K^+, Na^+, NH_4^+, Ca^{+2}, Mg^{+2}, Cl^-, SO_4^{2-}, NO_3^-, HPO_4^{2-}). Higher ash removal in the EFB compared to WS was the result of higher content of leachable inorganic fraction present in EFB. On comparing the results with the earlier published studies, ash removal in the present study was comparable to the removal seen after washing WS for 1–3 h (Singhal et al., 2021c). For EFB, it was even higher (12–16% more) than the removal seen after washing for 2 h with 10-times smaller sized sample (Lam et al., 2014).

3.1.2. Effect of step-washing on C, H, and O content, HHV, and energy loss

The improvement in the C, H, and O content from washing can be seen in Table 3. On increasing the washing steps, a continuous increment

Table 2
Effect of step washing (both with and without wastewater recirculation) on proximate composition, ultimate composition, heating values, mass, and energy yield (*nd = not detected*).

Washing type	Washing time for each step	No. of steps	MC (%)	VS (%)	FC (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)	HHV (MJ/kg)	Mass Yield (%)	Energy Yield (%)
						Wheat straw								
With fresh water only		Unwashed	3.06	73.02	15.68	8.24	43.64	5.60	0.50	0.05	42.02	17.31	–	–
	2 min	Single step	3.27	73.17	15.92	7.63	43.41	5.46	0.48	nd	43.02	16.97	96.62	94.75
		Two steps	2.65	74.04	15.95	7.36	43.90	5.58	0.44	nd	42.72	17.32	95.95	96.03
		Three steps	2.77	74.71	15.80	6.73	44.48	5.54	0.44	nd	42.81	17.48	95.45	96.41
	5 min	Single step	4.11	72.92	15.63	7.34	43.96	5.56	0.46	nd	42.68	17.32	95.45	95.54
		Two steps	3.47	74.22	15.59	6.71	44.99	5.60	0.41	nd	42.29	17.78	94.19	96.79
		Three steps	3.89	74.69	15.02	6.41	45.29	5.65	0.40	nd	42.26	17.96	93.75	97.28
	10 min	Single step	3.11	73.79	15.97	7.14	44.61	5.60	0.44	nd	42.21	17.65	96.17	98.08
		Two steps	3.87	73.77	15.25	7.11	45.25	5.68	0.39	nd	41.57	18.04	94.99	98.99
		Three steps	4.17	74.19	14.97	6.67	45.51	5.72	0.37	nd	41.73	18.17	93.32	97.96
With wastewater recirculation	5 min	Three steps	4.34	74.04	14.96	6.66	45.39	5.61	0.41	nd	41.94	17.97	94.46	98.07
		Three steps (at 40 °C)	5.17	74.51	14.06	6.27	45.63	5.71	0.38	nd	42.01	18.18	92.93	97.60
Pilot testing – with fresh water		Unwashed	8.20	71.90	10.20	9.70	44.00	5.30	0.55	0.14	40.40	17.91	–	–
	10 min	Single Step	8.51	73.90	8.99	8.60	45.60	5.60	0.49	0.09	39.80	18.09	–	–
Pilot testing – With wastewater recirculation	5 min	Two steps	7.12	74.70	9.68	8.50	45.40	5.60	0.42	0.06	39.90	18.11	–	–
		Two steps (at 45 °C	8.08	76.20	7.92	7.80	45.20	5.60	0.46	0.05	41.20	18.19	–	–
		After pressing	–	76.80	–	7.70	46.00	5.61	0.42	0.05	40.30	18.26	–	–
						Empty fruit bunches of oil palm								
With fresh water only		Unwashed	3.61	76.90	14.29	5.20	48.30	6.12	0.85	0.05	39.53	19.86	–	–
	2 min	Single step	3.12	77.95	15.36	3.57	48.28	6.18	0.67	nd	41.25	19.80	96.26	95.98
		Two steps	3.22	78.31	15.66	2.81	48.57	6.26	0.57	nd	41.79	19.94	92.82	93.18
		Three steps	3.18	78.86	15.09	2.87	49.11	6.33	0.46	nd	41.22	20.28	91.36	93.27
	5 min	Single step	3.24	78.26	15.22	3.28	48.81	6.19	0.58	nd	41.14	20.00	94.46	95.12
		Two steps	3.33	79.47	14.41	2.79	49.32	6.31	0.47	nd	41.10	20.34	91.84	94.06
		Three steps	3.38	79.44	14.50	2.68	49.75	6.36	0.40	nd	40.80	20.58	91.34	94.65
	10 min	Single step	3.15	78.60	14.99	3.26	49.13	6.26	0.57	nd	40.78	20.23	93.42	95.16
		Two steps	3.55	78.90	14.54	3.01	49.99	6.38	0.39	nd	40.23	20.74	90.99	95.01
		Three steps	3.25	79.73	14.24	2.77	50.16	6.39	0.40	nd	40.28	20.81	90.01	94.29
With wastewater recirculation	5 min	Three steps	1.96	80.51	14.84	2.69	49.87	6.35	0.44	nd	40.64	20.63	90.92	94.44
		Three steps (at 40 °C)	1.47	81.08	14.75	2.70	50.30	6.46	0.40	nd	40.15	20.96	88.84	93.74
Pilot testing – with fresh water	10 min	Unwashed	–	74.20	–	7.20	48.80	6.00	1.07	0.12	37.30	20.09	–	–
		Single Step	–	–	–	2.50	49.70	6.10	0.52	0.05	41.30	20.21	–	–
Pilot testing – With wastewater recirculation	5 min	Two steps	–	–	–	–	49.70	6.10	0.39	0.04	42.50	20.10	–	–
		Two steps (at 45 °C	–	82.10	–	1.90	49.90	6.10	0.40	0.03	41.80	20.24	–	–
		After pressing	–	83.00	–	1.70	49.90	6.10	0.42	0.03	42.00	20.23	–	–
Max st. dev			0.13	0.19	0.57	0.07	0.11	0.01	0.01	–	–	0.06	–	–

in C and H values was observed. For C, this increment was significant (<2% increment), while for H, this change was relatively smaller (<0.1% for WS and < 0.34% for EFB). Due to ash reduction and improvement in C–H values, an increment in HHVs was also seen in the washed samples, although the difference was minute (<1.1 MJ/kg). Increment in C and HHV content was also observed in the past washing studies. Though net increment in the value is highly variable, ranging between 0.5 and 8% and 0–3 MJ/kg respectively, depending on the biomass types (Deng et al., 2013; Mortari et al., 2021; Mu et al., 2021; Singhal et al., 2021c). A sudden reduction in the C and HHV values was noted in the 2 min washing case. This could be the result of the quick loss of some highly water-soluble organic compounds in the leachate. Earlier studies had also seen the leaching of some organic compounds from WS, such as sugars (mannose, xylose, glucose, cellobiose), organic acids (acetic acid, phthalic acid, propanoic acid, formic acid), and esters (phthalic acid esters) (Deng et al., 2013; Long et al., 2020; Yu et al., 2014). Due to the leaching of water-soluble compounds in each step, a certain mass loss is inevitable. However, due to the relatively low leaching of organics, energy losses in the step washing process were much lower compared to the single-step washing (3.5–17%) (Deng et al., 2013; Ma et al., 2018; Ma et al., 2017; Singhal et al., 2021b; Singhal et al., 2021c) and other pre-treatments, such as acid washing (10–18%), hydrothermal leaching (12–33%), and torrefaction (10–27%) (Cen et al., 2019; Chen et al., 2017; Madanayake et al., 2017). So, due to the increased C, H, and HHVs and lower energy losses, better performance can be expected from the step-washed biomass in the thermochemical processes.

3.1.3. *Effect of step-washing on the removal of troubling elements and indexes*

Both N and S are vital plant macronutrients, which are metabolised and incorporated into the organic structure of the biomass (Hawkesford et al., 2012). However, some N and S also present in mobile and water-leachable form, such as NO_3^-, NH_4^+, and SO_4^{2-}. Due to their high water-solubility, removal of up to 8–31% of N and 35–80% of S was observed in SWFW for WS while removal for EFB was 24–58% for N and 64–80% for S. Due to the higher net content and soluble-fraction of N and S, higher removal of these elements was seen in EFB compared to WS. Higher removal was seen for both the elements on increasing the washing steps. A possible explanation for such a high removal of N and S could be the enhanced diffusion of both the elements due to removal of the leachate in each washing step. The best N and S removal achieved for WS in the present case (10 + 10 + 10 min) was even better than single-step washing for 3–24 h (Jenkins et al., 1996; Singhal et al., 2021b).

Table 3

Effect of step-washing with (SWWR) and without wastewater recirculation (SWFW) on the ash composition (wt%) and indexes for WS and EFB (*colour code: Dark red – extreme; Light red – high; Yellow – Medium; Green – Low fouling/slagging*).

Washing type	Washing time for each step	No. of steps	SiO_2	K_2O	Cl	MgO	P_2O_5	SO_3	CaO	Fe_2O_3	Al_2O_3	Na_2O	TiO_2	B/A	AI	Cl_i	S_i
Wheat straw																	
		Unwashed	29.97	16.33	8.55	4.66	1.75	0.77	1.52	0.11	0.30	0.11	nd	0.82	0.78	0.70	82.5
With fresh water only	2 min	Single step	35.99	13.56	3.3	4.40	2.18	0.55	1.69	1.00	0.35	nd	nd	0.64	0.61	0.25	83.5
		Two steps	38.87	12.83	2.06	3.92	2.13	0.48	1.68	0.99	0.35	nd	nd	0.55	0.54	0.15	85.5
		Three steps	44.84	10.41	0.57	3.42	2.60	0.40	1.95	1.27	0.37	nd	nd	0.44	0.40	0.04	87.1
	5 min	Single step	37.12	13.24	3.16	3.51	1.95	0.55	1.68	0.86	0.35	nd	nd	0.57	0.56	0.23	85.9
		Two steps	42.64	11.41	0.86	3.89	2.18	0.43	1.86	1.08	0.39	nd	nd	0.48	0.43	0.06	86.1
		Three steps	48.75	9.02	0.35	3.18	2.65	0.30	2.10	1.40	0.39	nd	nd	0.38	0.32	0.02	87.9
	10 min	Single step	38.84	12.71	1.84	3.26	2.05	0.49	1.87	0.94	0.35	nd	nd	0.54	0.51	0.13	86.5
		Two steps	47.18	9.37	0.46	2.99	2.74	0.38	2.14	1.32	0.38	nd	nd	0.39	0.37	0.03	87.9
		Three steps	50.45	7.82	0.37	3.99	2.54	0.25	2.14	1.37	0.38	nd	nd	0.35	0.29	0.02	87.1
With wastewater recirculation	5 min	Three steps	48.76	8.92	0.42	2.90	2.15	0.29	1.81	1.17	0.38	nd	nd	0.35	0.33	0.03	89.2
		Three steps (40 °C)	51.45	7.88	0.25	3.04	2.31	0.28	1.98	1.27	0.45	nd	nd	0.33	0.29	0.02	88.9
Empty fruit bunches of oil palm																	
		Unwashed	16.35	29.02	15.1	5.89	1.43	1.62	1.24	7.22	0.56	0.20	0.22	2.66	0.77	0.79	53.2
With fresh water only	2 min	Single step	26.09	27.30	4.19	7.45	2.28	0.88	1.92	4.44	0.59	0.06	0.22	1.63	0.49	0.15	65.4
		Two steps	36.06	22.53	1.47	10.62	3.08	0.82	2.39	6.69	0.45	nd	0.22	1.24	0.32	0.04	64.7
		Three steps	37.81	21.22	0.93	10.67	3.24	0.74	3.00	6.32	0.73	nd	0.22	1.15	0.31	0.03	65.4
	5 min	Single step	30.06	24.61	2.47	6.47	2.46	0.79	2.52	5.07	0.47	nd	0.03	1.35	0.40	0.08	68.1
		Two steps	39.12	20.93	0.45	9.99	3.06	0.68	2.93	7.07	0.72	nd	0.03	1.10	0.29	0.01	66.2
		Three steps	39.37	20.57	0.51	11.46	2.91	0.71	2.57	6.82	0.73	nd	0.03	1.10	0.27	0.01	65.4
	10 min	Single step	34.98	22.13	1.47	6.52	2.69	0.71	2.25	6.17	0.86	nd	0.02	1.11	0.36	0.05	70.1
		Two steps	42.49	18.07	0.46	11.62	3.48	0.68	3.61	6.14	0.72	nd	0.03	0.99	0.26	0.01	66.6
		Three steps	41.75	21.28	0.34	8.02	3.16	0.67	2.97	6.38	0.70	nd	0.02	0.98	0.28	0.01	70.6
With wastewater recirculation	5 min	Three steps	43.35	18.45	0.11	10.05	2.98	0.78	3.21	7.99	0.49	nd	0.03	0.98	0.24	0.01	66.8
		Three steps (40 °C)	47.21	18.25	0.21	10.99	3.11	0.81	2.90	7.78	0.54	nd	0.03	0.90	0.23	0.01	68.5

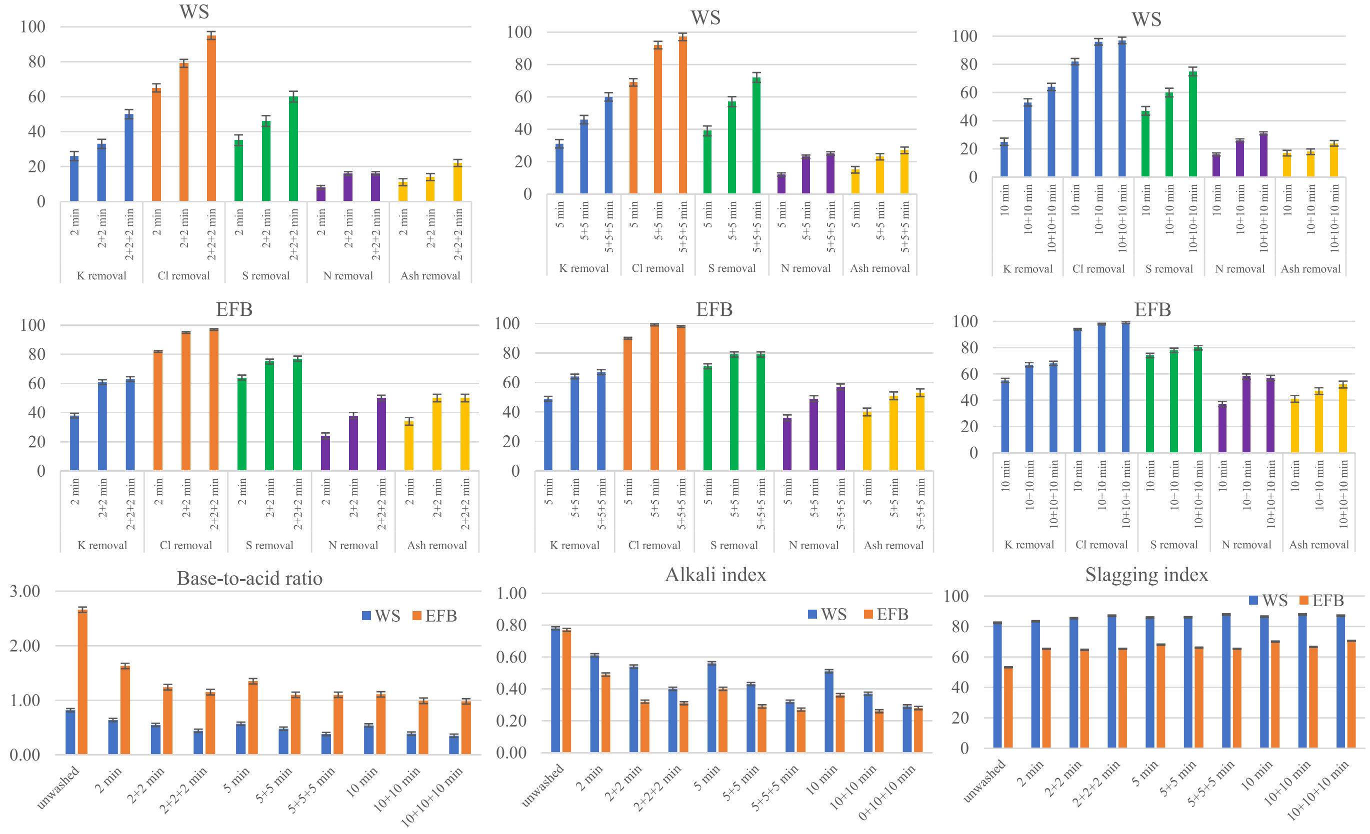

Fig. 2. Effect of step washing with fresh water (SWFW) on removal of troubling elements and different indexes.

Very high to substantial removal of troubling elements such as Na (∼100%), Cl (65–99%), S (35–80%), K (26–68%), N (8–57%), Mg (9–53%), and P (0–10%) was seen in the step-washed samples. Most of these elements form several water-soluble and weakly bound compounds during epigenesis, such as KNO_3, $NaNO_3$, KCl (sylvite), NaCl (halite), K_2SO_4 (arcanite), Na_2SO_4, K_3PO_4, and $Ca(NO_3)_2$ (nitrocalcite), which leach in higher amounts on washing (Niu et al., 2016; Vassilev et al., 2012; Vassilev and Vassileva, 2019). Except for the 2 min single-step washing case, almost complete removal of Na was seen for both types of biomasses. Higher removal of K and Cl was seen in EFB compared to WS, due to the higher total and soluble content of these elements present in EFB (Fig. 2). From the ash analysis (Table 3) and leachate analysis (Table 4), it was evident that most of the K and Cl in EFB was already leached in the first step. The reduction was small in the second step and negligible in the third step for EFB (Fig. 3). Similar to N, S, and ash removal, the highest removal of K (64–68%) and Cl (97–99%) for both types of biomasses was also achieved in the case 10 + 10 + 10 min, though removal efficiencies were similar to the case 5 + 5 + 5 min. In past studies, even after washing WS for 6–24 h, Cl removal was 6–40% less than the present case (Deng et al., 2013; Singhal et al., 2021b; Singhal et al., 2021c). According to Singhal et al. (2021a) and Ma et al. (2017), Cl removal seems to be negatively affected by competition between the ions, which is more potent in the single-step washing cases. The use of fresh water in each washing step could be the major reason behind the higher removal of Cl in SWFW. According to past studies, to achieve 60% of K removal, WS needs to be washed for 3 h with a 3–5 cm size and for 30–60 min with a 0.05–0.08 cm size (Singhal et al., 2021c). K removal in the present case was 3–16% less for WS and 2–15% less for EFB compared to the few washing studies that used longer washing durations (6–24 h) with a much smaller feedstock size (0.28–0.90 μm) (Deng et al., 2013; Yu et al., 2014). Around 5–20% of K, 2–15% Ca, and 0–10% P in WS is ion exchangeable (Zevenhoven et al., 2012), which is partially leached in single-step washing due to leached organic compounds. However, as the continuous washing duration was small (≤10 min) and the leachate was also removed in every step, the leaching possibility for these ion-exchangeable species was very less in the present case. This could be the possible reason behind the lower removal of K and no removal of Ca and P. Still, the removal seen for K, Na, and Cl in the present study is very high. Consequently, lower fouling, slagging, and corrosion can be expected from the washed feedstock, as these elements are the main culprits behind such issues.

As per Cl%, a lower slagging and corrosion tendency can be expected from both the feedstocks after washing for just 6–10 min in step washing. On increasing the washing steps, a continuous reduction in the AI and B/A was observed for both feedstocks. As per AI, severe fouling can be expected from the untreated EFB and WS, which showed a two-fold reduction after step-washing. Still, even with the lowest AI scenario, low to medium fouling can be expected for both feedstocks. As per B/A, lower fouling tendencies were seen in WS, though the AI for both types of feedstocks is very similar. One important fact that should be considered when examining the above-mentioned indexes is that they were originally developed for coal (Garcia-Maraver et al., 2017; Niu et al., 2016). Thus, the cut-off values of these indexes may not be directly applicable to agricultural residues due to differences in the elemental composition (Niu et al., 2016; Vassilev et al., 2015, 2010). For biomass, they often lead to overestimations, as they do not consider the effect of ash, Cl, and S (Zevenhoven et al., 2012). Consequently, instead of looking at the cut-off values, more preference should be given to the trends in the indexes, which are very promising in the present study. Thus, due to the very high removal of Cl (<99%) and S (<80%) together with K (<70%) and Na (∼100%), much less fouling, corrosion, and slagging should be expected for the washed biomass.

After comparing all the results for both WS and EFB, the 10 + 10 + 10 min case shows the best results, albeit only marginally (0–6%)

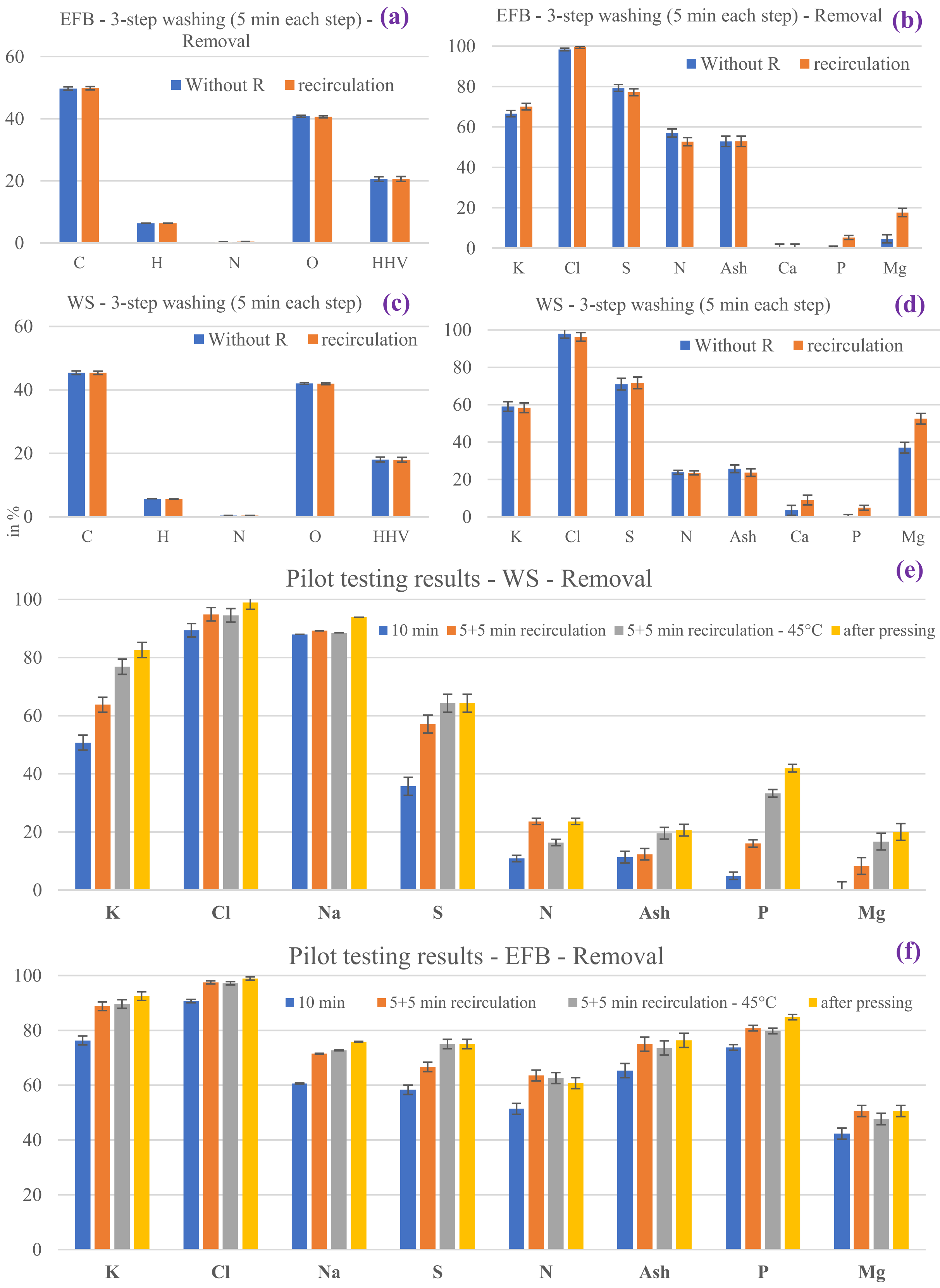

Fig. 3. Comparison between step washing with (SWWR) and without wastewater recirculation (SWFW) (a) and (b) for EFB; (c) and (d) for WS; (e) and (f) pilot testing results of SWWR.

Table 4
Results of the characterisation of wastewater resulting from the pilot testing of WS washing.

Washing Time	10 min	5 + 5 min (at 25 °C)		5 + 5 min (at 45 °C)			Max St. dev
	Single-step	Step 1	Step 2	Step 1	Step 2	Pressing leachate	
COD (mg/l)	2460	4080	1520	4980	1100	6250	113
BOD (mg/l)	620	1100	320	1300	470	2700	43
EC (mS/cm)	1.26	2.11	0.752	2.38	0.686	2.14	0.10
pH	6.90	6.60	7.00	6.40	6.80	5.90	0.12
K (mg/l)	339.60	593.00	192.30	678.40	176.30	502.30	19.61
Na (mg/l)	10.64	8.12	8.80	4.78	4.50	180.60	1.83
P (mg/l)	10.32	17.92	5.90	21.61	5.86	250.20	1.01
Cl^- (mg/l)	100.00	190.00	43.00	200.00	27.00	47.00	4.57
Total N (mgN/l)	62	110	36	130	38	210	3.55
NH_4^+ (mg/l)	14	28	9.3	38	11	51	–
NH_4-N (mgN/l)	11	21	7.2	30	8.8	40	–

compared to the 5 + 5 + 5 min case. For practical purposes, 5 + 5 + 5 min washing should therefore be preferred, as it saves 15 min with almost the same improvement. For EFB, for almost all the parameters, much less removal was seen in the third washing step. So, 2 + 2 + 2 min or 5 + 5 min washing cases should be used for practical applications. One major limitation with the SWFW process was the requirement of thrice the amount of water needed in the single-step washing. For large-scale operations, this high demand for fresh water and consequently higher quantities of wastewater generated will be a major issue. For that reason, step-washing process was further optimised by reusing the wastewater (SWWR) for washing process.

3.2. Effect of step washing with wastewater recirculation (SWWR)

The most interesting outcome of the present study was that even when washing with one-third the amount of water used in SWWR, the removal efficiencies were almost the same as SWFW (Fig. 3). For both feedstocks, ultimate composition, HHV, and removal of troubling elements in the SWWR case were almost the same as the previous case where only fresh water was used. Before the experiments were conducted, a lower washing efficiency was expected from the SWWR process because it was assumed that the reuse of wastewater may negatively affect the leaching of water-soluble species. However, as per the results, it seems incorrect, as the efficiency of SWWR is similar to SWFW. Furthermore, extra removal was seen for Mg (3–16% more), Ca (0–5% more), P (4–9% more), and K (0–4% more), which was not seen earlier in SWFW. There could be two main reasons behind the high removal of these elements. First, this extra leaching of troubling elements could be due to the effect of organics present in leachate, as explained in the previous section. This phenomenon was most profound for longer washing durations, as seen in earlier washing studies on WS (Singhal et al., 2021c) and mallee wood (Liaw and Wu, 2013). The extra leaching of K, Ca, P, and Mg in SWWR is proof that leached organics also play a significant role in enhanced leaching, which can be verified from the wastewater testing results. The second possible reason behind the high removal of other troubling species could be utilizing a sufficient amount of water for washing. Some highly water-soluble species (K^+, Cl^-, NO_3^-, and SO_4^{2-}) leach in considerable amounts in the first and second steps due to the sufficient S:L ratio, even though there is higher competition between ions for leaching. It is very likely that both phenomena happen in parallel and result in the higher removal of the troubling elements in SWWR. For further explanation, identification of organic species and inorganic elements in the leachate is essential, which is ongoing in our lab (see the last section). As K, P, Ca, and Mg directly and indirectly participate in fouling and slagging in combustion and gasification (Chin et al., 2015; Link et al., 2012), lower deposition issues can be expected from the washed feedstocks due to their higher removal. Furthermore, higher ash and alkali content negatively affects bio-oil yield and stability obtained from the slow-pyrolysis (Bhatnagar et al., 2021). So, better yields and quality of the bio-oil can be expected form the washed WS and EFB due to high removal of alkali elements and other inorganics, which was observed in (Chen et al., 2017; Mortari et al., 2021). On comparing indexes, B/A values for both the feedstock remain the same, while AI and S_i show a slight improvement in SWWR compared to SWFW. Another benefit of SWWR is the higher mass and energy yields, which are 1.5 to 6.5 times better than SWFW and past washing studies (Deng et al., 2013; Ma et al., 2018; Ma et al., 2017). Smaller mass loss with an increment in C% means that even fewer organics were leached in the SWWR compared to SWFW and single-step washing.

To attain such high improvement in the composition of biomass observed in SWWR, biomass needs to be washed for at least 3 to 24 hrs (Jenkins et al., 1996; Ma et al., 2017; Singhal et al., 2021c; Yu et al., 2014). Washing time is a major constraint for industrial operation, as it easily leads to a larger reactor size and lower productivity (Singhal et al., 2021b). When looking at these aspects, SWWR shows the best pre-treatment efficiency thus far achieved in much shorter durations (just 8–15 min) and with the same amount of water required in the single-step washing. Due to these benefits, SWWR with 5 + 5 + 5 min is highly recommended for large-scale applications. To further improve the washing efficiency, washing temperature can be further increased. SWWR at 40 °C shows even better removal of K, Cl, S, and ash for both feedstocks compared to 20 °C (Fig. 3). Consequently, even lower B/A, AI, Cl%, and higher S_i were observed. For single-step washing, in past studies also a similar improvement in washing efficiency was seen on increasing the washing temperature (Bandara et al., 2020; Deng et al., 2013; Singhal et al., 2021b). To further improve the efficiency in SWWR, washing temperatures (>60 °C) and durations (>15 min) can be increased with a smaller feedstock size (≤1 cm). However, in such cases, more energy demand, greater energy losses, and higher equipment costs should be expected for practical applications.

3.3. Pilot-scale testing results

As SWWR results in high washing pre-treatment efficiencies, pilot testing was conducted to check its effectiveness in a larger-scale replica. The SWWR case of 5 + 5 min was tested for the pilot study, and the washed samples were evaluated for chemical composition and wastewater quality. Similar to the experimental results, pilot testing of SWWR also shows much better improvement in feedstock quality compared to single-step washing for the same washing duration. Very high to substantial removal of K, Cl, Na, S, and N was seen in the pilot testing of both feedstocks, similar to the lab-scale testing (Fig. 3e and f). Similar to earlier SWWR experiments, the leached organics also seem to play a significant role in this case as well. As a result, the higher removal of K (18–25% more), P (7–28% more), and Mg (8–17% more) was noted in both feedstocks, which were earlier leached in relatively smaller amounts in the single-step washing and SWFW. Due to the high removal of these troubling elements during the pilot testing, much lower fouling, slagging, and corrosion can be expected from the washed biomass as per the indexes. Compared to the lab experimental case of 5 + 5 min without recirculation, the results of the pilot testing are similar to better for most of the elements (Fig. 3). Therefore, as per the pilot-testing results, it can be confirmed that SWWR will result in high washing efficiencies even in large-scale operations. For additional efficiency, washing can be done at a higher water temperature. Samples washed at 45 °C show even higher removal of K (1–13% more), S (7–9% more), ash (0–7% more), P (0–17% more), and Mg (0–8% more) than washing at 25 °C (Fig. 3).

Another more efficient alternative could be mechanical pressing of the washed biomass. Due to pressing, up to 0–10% extra removal of troubling elements was seen specially for K, Cl, and P (Fig. 3e). During washing, biomass may soak water up to 2.5–3 times its original weight. Thus, pressing can have dual benefits, as it reduces the moisture content of the washed feedstock (<40% reduction) and remove extra troubling elements remaining in the aqueous phase. Thus, for industrial applications, SWWR washing with two or three steps is recommended with mechanical pressing of the washed feedstock.

3.4. *Wastewater characterisation*

On analysing wastewater, the effect of each washing step can also be verified from the EC, K^+, and Na^+ concentration values mentioned in supplementary material. In addition, these values were even higher for SWWR due to the reuse of murky water to further remove the impurities and soluble compounds. EC, K^+, and Na^+ values of the EFB washing leachate were relatively higher compared to those for WS. This was due to the higher leaching of troubling elements in EFB on washing, which was also seen in the fuel analysis results. As highly soluble organic and inorganic species quickly leach into the water (<10 min), the first step of the step-washing process has the highest EC, K^+, and Na^+ values. The results of the pilot wastewater characterisation are described in Table 4. Similar to lab-scale washing, the first step results in the higher leaching of troubling elements and soluble organics than the next step in the pilot testing. Consequently, the wastewater generated in the first step was murkier and had a much higher COD, BOD, and concentration of troubling elements. On increasing the washing step, a higher removal of K, Cl, Na, N, and P was achieved earlier in WS due to which substantial amounts of these elements were also seen in step two of SWWR.

Another interesting outcome seen was the positive correlation of K and P content with COD and BOD in wastewater. This is the proof of an earlier observation, i.e. leached organics result in higher removal of weakly bound and/or ion exchangeable species. It was already explained earlier that increasing the washing temperature results in better removal of troubling elements with higher organic losses. Subsequently, the wastewater resulting from this case had an even higher concentration of COD, BOD, and troubling elements. On increasing the washing temperature, higher COD and concentrations of K, Na, and P were also seen in Deng and Che (2012). The wastewater resulting from the mechanical pressing of the washed feedstock was much less in quantity, but had the highest BOD, COD, and inorganics concentration. As pressing is highly beneficial and the wastewater result from it is very low in quantity, pressing leachate can be diluted with the washing leachate and treated together.

Compared to past studies, COD values in the present study were 7–8 times and 2.5 times higher compared to the findings of Deng and Che (2012) (WS used) and Jenkins et al. (2003) (rice straw), respectively. Wastewater effluent from step-1 was used for washing untreated feedstock twice, due to which it was dirtier than any other past washing processes. Also, as shown by Liaw and Wu (2013) and Deng and Che (2012), soluble organics are first to leach on washing. This could be another reason behind the higher COD and BOD values in the present case. Compared to past studies on WS (Deng and Che, 2012; Yu et al., 2014), a much higher concentration of K, P, Mg, N, and S was observed in the wastewater of SWWR case. These higher values of the troubling elements in the wastewater are coherent with the findings of the previous section.

Based on the various parameters analysed in the leachate, some preliminary ideas regarding wastewater treatment can be suggested for industrial-scale applications. As spent water from washing contains a high concentration of plant nutrients (K, N, P), it can be used in agricultural fields for nutrient recycling. However, due to the high COD and BOD of the wastewater, it needs to be treated first to meet discharge standards (Vassilev and Vassileva, 2019). Furthermore, analysis of heavy metals in the leachate should be taken into consideration, as they may contaminate the environment if present in higher concentration. As BOD in the present study is much less compared to COD (3.7–3.9 times), biological treatments such as activated sludge process and anaerobic digestion may not be feasible in the present conditions. However, membrane filtration and chemical oxidation processes may be used for the treatment. Electrochemical advanced oxidation processes (EAOP) with nutrient recovery (Sirés et al., 2014) and reverse osmosis (RO) (Jenkins et al., 2003) may be some potential treatment options for such types of wastewater. However, treating large amounts of wastewater with RO and EAOP may result in higher capital and operational costs, with extra issues related to membrane fouling and disposal of the rejected waste. These high costs could be a bigger threat to the feasibility of the overall washing process, as the cost benefits provided by the washing may be overcome by the greater expenses of the wastewater treatment. Another possible approach for treatment could be the transformation of non-degradable organics in the wastewater into biodegradable fractions using chemical oxidation or ozonation. Biological treatment may then become more feasible due to the high nutrient content of the wastewater. Another possibility is that EFB washing leachate can be combined with Palm oil mill effluent for sugar production (Tang et al., 2020). Regardless, such ideas require further modification and actual testing for better results. Furthermore, to improve technical feasibility, further characterisation of wastewater is also required. Evaluation of parameters such as soluble COD, TOC, total and volatile suspended solids (TSS and VSS), heavy metal analysis, and ionic concentration will definitely assist in evaluating the feasible treatment options for wastewater. A detailed analysis of wastewater and washing LCA and TEA studies are currently ongoing at our lab, and it will be presented as a separate study. The main aim of the present study was to evaluate the quality of wastewater and to arrive at a preliminary idea about potential wastewater treatment options. As it was earlier missing from the literature, present study definitely helps to draw a clear picture of wastewater quality, handling, and treatment-related issues for industrial-scale washing.

4. Conclusion

A novel and modified washing process was designed and tested: multiple-step washing with (SWWR) and without (SWFW) wastewater recirculation. SWFW resulted in high ash, Cl, S, K, and N removal. Consequently, much lower fouling, slagging, and corrosion propensities were noted after pretreatment. Even with a third of the amount of fresh water, SWWR is more effective than SWFW. Single-step washing requires 6–24 h of washing to attain comparable removal as SWWR. The pilot testing results showed high removal efficiencies even on a larger-scale. Higher content of COD, BOD, K, Cl, and N was seen in wastewater, requiring special attention.

CRediT authorship contribution statement

Abhishek Singhal: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Visualization, Writing - original draft. **Maria Goossens:** Methodology, Project administration, Formal analysis, Validation, Writing - review & editing. **Davide Fantozzi:** Investigation, Methodology, Writing - review & editing. **Antti Raiko:** Formal analysis, Methodology, Resources. **Jukka Konttinen:** Conceptualization, Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing. **Tero Joronen:** Conceptualization, Methodology, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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