Designer Biochar-Coke Mixtures to Remove Naphthenic Acids from Oil Sands Process-Affected Water (OSPW)

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REPORT SUMMARY

The objective of this 6-month pilot experimental study was to test the ability of biochars derived from Alberta biomass and an oil sands petroleum coke to remove selected organic acids from water. To this end, we selected one biochar produced from wheat straw and made by the Alberta Biochar Initiative, and an oil sands petroleum coke produced by Syncrude Canada Ltd. Both materials were extensively characterized for morphology, surface area, surface reactivity, porosity, and composition. Following this characterization, two model organic species, lauric acid and 1-methylcyclohexanecarboxylic acid, were adsorbed to the biochar, coke, and mixtures of the two, at varying ratios.

Our results indicate that the biochar used in this study is a significantly more efficient sorbent for removal of both organic acids tested from water than is the petroleum coke. The petroleum coke was found to remove a lower but significant amount of each organic acid from solution. The use of petroleum coke as a sorbent will likely depend on environmental risks such as the leaching of sulphur, vanadium, and nickel from the material, and its cost relative to the production and delivery of biochar to oil sands facilities.

Future studies should focus on assessing the total sorption capacity of each sorbent in flow-through reactor experiments, and determining whether combined biochar + petroleum coke systems may be efficient at removing both organic contaminants and metals from oil sands process-affected water.

ACKNOWLEDGEMENTS

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1 INTRODUCTION

Oil sands process-affected water (OSPW) contains a wide range of dissolved organics that may pose risks to aquatic ecosystems and human health (He et al. 2012)[1]. In particular, naphthenic acids[2] (NAs) extracted into the water during the upgrading process pose substantial risks to freshwater aquifers and aquatic ecosystems (Ahad et al. 2013). NAs are known to accumulate in aquatic organisms including fish (Leung et al. 2003, Peters et al. 2007) and can be passed to mammals, causing chronic health effects (Cruz-Martinez and Smits 2012, Rogers et al. 2002).

In this project, we assessed the ability of two materials, a wheat straw (WS) biochar produced by the Alberta Biochar Initiative[3] and a Syncrude petroleum coke (SPC), to remove two model organic acids from solution. The two treatment materials are attractive for different reasons:

- Oil sands petroleum coke is a byproduct of the processing of oil sands, and is abundantly available at sites with upgraders. Although coke is considered a resource in Alberta, it is not yet widely used as a fuel, largely due to its high sulfur content. Further, it contains heavy metals such as vanadium and nickel and burns dirtier than conventional coal (Oil Change International 2013). However, it may prove a good adsorbent for certain types of NAs depending on its activation and solution (pH, water chemistry) conditions (Gamal El-Din et al. 2011).

- Biochars are the byproducts of the carbonization and/or pyrolysis of many types of biomass, yielding a stable, high surface area, carbon-rich product proven to be effective in the removal of organic and metal contaminants from water (Ahmad et al. 2013b). They are proven in the removal of a wide range organics from water, including chlorinated ethenes, PAHs, and other hydrophobic organic contaminants (Ahmad et al. 2012, Ogbonnaya and Semple 2013).

Here we chose two model organic acids, lauric acid and 1-methylcyclohexanecarboxylic acid, and conducted adsorption experiments with WS and SPC at various ratios of acids to sorbents, and at a pH (8.65) relevant to OSPW. Prior to the adsorption experiments, each material was characterized extensively for morphology, surface area, porosity, and reactivity. Using the characterization information and the results of the organic acids sorption experiments, we discuss the relative appropriateness of using each sorbent, or combinations of the two sorbents, for removing organics from OSPW. This information will provide valuable information to operators

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[1] For more information on other OSPW constituents, especially inorganic components, see Li, C., A. Singh, N. Klamerth, K. McPhedran, P. Chelme-Ayala, M. Belosevic and M. Gamal El-Din, 2014. Synthesis of Toxicological Behavior of Oil Sands Process-Affected Water Constituents. OSRIN Report No. TR-50. 101 pp. http://hdl.handle.net/10402/era.39659

[2] For more information on naphthenic acids see Zhao, B., R. Currie and H. Mian, 2012. Catalogue of Analytical Methods for Naphthenic Acids Related to Oil Sands Operations. OSRIN Report No. TR-21. 65 pp. http://hdl.handle.net/10402/era.26792

[3] See http://albertabiochar.ca/

to optimize the types and amounts of sorbents in bioreactors at oil sands facilities under specific process conditions.

2 MATERIALS AND METHODS

2.1 Chemical and Reagents

Hydrochloric acid (HCl), Sodium bicarbonate ($NaHCO_3$), Sodium carbonate (Na_2CO_3), Sodium hydroxide (NaOH), Calcium chloride ($CaCl_2$), Barium chloride ($BaCl_2$) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were all analytical grades and purchased from Fisher Scientific. Two naphthenic acids: lauric acid and 1-methylcyclohexanecarboxylic acid[4] were purchased from Sigma Aldrich (Milwaukee, USA). Stock solutions were prepared using ultrapure water (18.2 MΩ cm^{-1} resistivity at 25°C).

2.2 Biochar and Petroleum Coke Production

Biochar produced from wheat straw (WS) was collected from the Alberta Biochar Initiative (ABI). The biomass from wheat straw was pyrolyzed at 600°C using a 12″ Auger Retort Unit, capable of processing biomass which contains a moisture content of up to 60%.

Syncrude produces fluid coke which is composed of fine particles, and uses a ~350°C temperature during the upgrading process. A Syncrude petroleum coke (SPC) collected from Syncrude’s processing plant site was used in this study.

2.3 Biochar and Petroleum Coke Characterization

The moisture contents of WS and SPC were estimated using a drying oven (ThermoScientific HERATHERM) held at 105°C for 24 hours according to the method of Ahmad et al. (2013a). The elemental compositions of WS and SPC, including C, N, H, S, and O, were determined using a Carlo Erba EA1108 Elemental Analyzer. This instrument combusts solid materials at 1,000°C. Molar ratios of H/C and O/C were calculated using the elemental composition data of C, H and O.

The specific surface area, pore volume and pore diameter of WS and SPC were estimated using an Autosorb Quantachrome 1MP, according to the Brunauer-Emmet-Teller (BET) and the Barret-Joyner-Halender (BJH) methods. The samples were degassed at 423 K for 8 hours and were characterized by N_2 adsorption.

We used a Zeiss EVO MA 15 LaB_6 filament scanning electron microscope, at magnifications ranging from 61× to 875× with a resolution of approximately 5 mm to obtain high resolution images and elemental compositions of WS and SPC samples. Carbon coated samples were coated with a Leica EMSCDE005. Backscattered images were taken using a Si diode detector. Energy dispersive X-ray spectroscopy (EDS) data were acquired with a Peltier-cooled 10 mm^2

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[4] Sometimes written 1-methylcyclohexane carboxylic acid

Bruker Quantax 200 Silicon drift detector with 123 eV resolution. Secondary electron images were obtained using a Everhart-Thornley detector.

2.4 Boehm Titrations

The modified Boehm titration method (Fidel et al. 2013) was used to determine the concentrations of acidic functional groups in WS and SPC. Briefly, WS and SPC were sieved at <0.5 mm (No. 35 mesh). Sieved WS and SPC were shaken for 24 h in a solution of 0.05M HCl, then washed twice with 1M $CaCl_2$, and finally washed four times with deionized water. All of the above washing steps were conducted at a 50:1 solution volume to biochar mass ratio. The samples were dried for ~ 60 h at 50° C. 0.5 g samples of this pre-treated material were added to 25 ml of the three bases used in the Boehm method ($NaHCO_3$, Na_2CO_3 and NaOH) at 0.05 M, and shaken for 24 hours. Aliquots were then taken and passed through 0.45-µm nitrocellulose filter paper using a Büchner funnel apparatus. To remove DOC and carbonate ions, the separated aliquots were mixed thoroughly with an equivalent volume of 1M $BaCl_2$ solution. Finally, 0.05 M and 0.01 M NaOH were added to the extracts of $NaHCO_3$ and Na_2CO_3, so that the NaOH:$BaCl_2$:extract ratio was 1:1:1. These samples were centrifuged at 8,000 g for 30 min and the resulting supernatants were filtered through 0.02-µm membranes (Anatop). The resulting aliquots were acidified to pH < 2 and then titrated with standardized 0.01M NaOH using a Titroline 6000 titrator (SI Analytics, Mainz, Germany). All treatments above were also performed on water blanks, and the resulting blank values were subtracted from experimental values.

The concentrations of acidic functional groups were determined by considering that $NaHCO_3$, Na_2CO_3 and NaOH would neutralize different acids. $NaHCO_3$ neutralizes strong acids (carboxylic), Na_2CO_3 neutralizes low pKa phenols and lactones (moderate acids) and NaOH neutralizes high pKa phenols (weak acids) (Goertzen et al. 2010).

2.5 Potentiometric Titrations

Potentiometric titrations were performed on WS and SPC. For each titration, approximately 1 g of material (weighed exactly[5]) was added to 50.0 ml of 0.01 M NaCl. While stirring, microlitre volumes of 12 M HCl were added to the resulting mixture until the solution pH reached approximately 4. The samples were titrated, using the Titroline 6000 instrument, by adding small volumes of 1.0 M NaOH, recording the resulting pH after equilibrium was reached, and repeating until pH 11 was achieved. Acidity constants (pK_a) and site concentrations for surface functional groups were solved for using FITEQL 4.0 (Herbelin and Westall 1999), a least squares optimization data fitting program.

2.6 Organic Acids Adsorption Experiments

Adsorption experiments were performed to determine the sorptive capacity of WS and SPC for two organic acids (OAs) as a function of OA and sorbent concentrations at a fixed pH (8.65)

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[5] 1 g of sample is targeted but the exact weight (e.g., 0.983 g) must be determined for use in subsequent calculations.

similar to that of OSPW (Gamal El-Din et al. 2011). Lauric acid and 1-methylcyclohexanecarboxylic acid adsorption experiments were conducted at concentrations of 0.025 to 25 mg L^{-1}, with WS, SPC, and 1:1 mixtures by mass of WS and SPC, at concentrations between 0.1 and 20 g solids L^{-1} solution, in 10 mL borosilicate test tubes. The pH was held constant by adding 0.1 M HEPES buffer adjusted to pH 8.65 to the experiments. Experimental test tubes were placed on a rotary shaker for 24 h, and afterward centrifuged for 30 min at 8,000 g to remove solids from solution.

The resulting supernatants were passed through 0.45 µm filters (Millex HP), and concentrations of OAs in the filtrates were determined using high performance liquid chromatography – mass spectrometry (HPLC-MS). HPLC-MS analyses were performed at the Devon (Alberta) Research Centre of Natural Resources Canada, according to methods published in Wang and Kasperski (2010). The difference between the concentration of NA initially added to the solution in an experiment and the amount remaining in the supernatant after equilibration was assumed to be adsorbed to the solids.

2.7 Adsorption Model

A distribution coefficient (K_D) isotherm approach was used to model the extent of adsorption of NAs onto WS and SPC. The equilibrium sorption capacity was estimated according to the method of Ahmad et al. (2013), using the following equation:

$$Q_e = [C_0 - C_e]VM^{-1} \qquad (1)$$

where,
Q_e = amount of NAs adsorbed on adsorbent at equilibrium (mg/g),
C_0 = initial concentration of NAs in solution (mg/L),
C_e = concentration of NAs in solution at equilibrium (mg/L),
V = total volume of the solution (L), and
M = mass of adsorbent used (g).

In this way, the linear isotherm model is expressed as:

$$Q_e = K_D C_e \qquad (2)$$

where K_D is the linear partitioning coefficient.

3 RESULTS AND DISCUSSION

3.1 Materials Characterization

3.1.1 *Electron Microscopy and Energy Dispersive X-Ray Spectroscopy*

Major differences in the morphology and reactivity between the biochar (WS) and oil sands petroleum coke (SPC) were uncovered during the characterization of these materials, which included light microscopy (Appendix 1) and scanning electron microscopy (SEM). SEM studies of the SPC indicate that the material is comprised primarily of semi-spherical, smooth beads of approximately 100 to 200 µm in diameter, although larger agglomerates of these beads on the millimetre scale are present (Figure 1). While the washing procedure (see section 2.4) caused no visible changes in the morphology of individual SPC beads (Figure 1B versus 1D), some loss of the cement holding together agglomerates was observed in the washed sample (Figures 1A versus 1C). Qualitative information about the elemental composition of SPC were collected using energy dispersive X-ray spectroscopy (EDS) at specific points on each sample, indicated by red numbers appearing in Figures 1A and 1C. Those measurements show that SPC is composed primarily of C, S, and O, in agreement with the separate elemental analysis data (see below), and that significant concentrations (> 0.1%) of Si, Al, Fe, Ti, Ca, K, and Na are also present (see Appendix 2). No significant differences in elemental composition were observed between EDS data collected on individual beads and cemented agglomerates of beads.

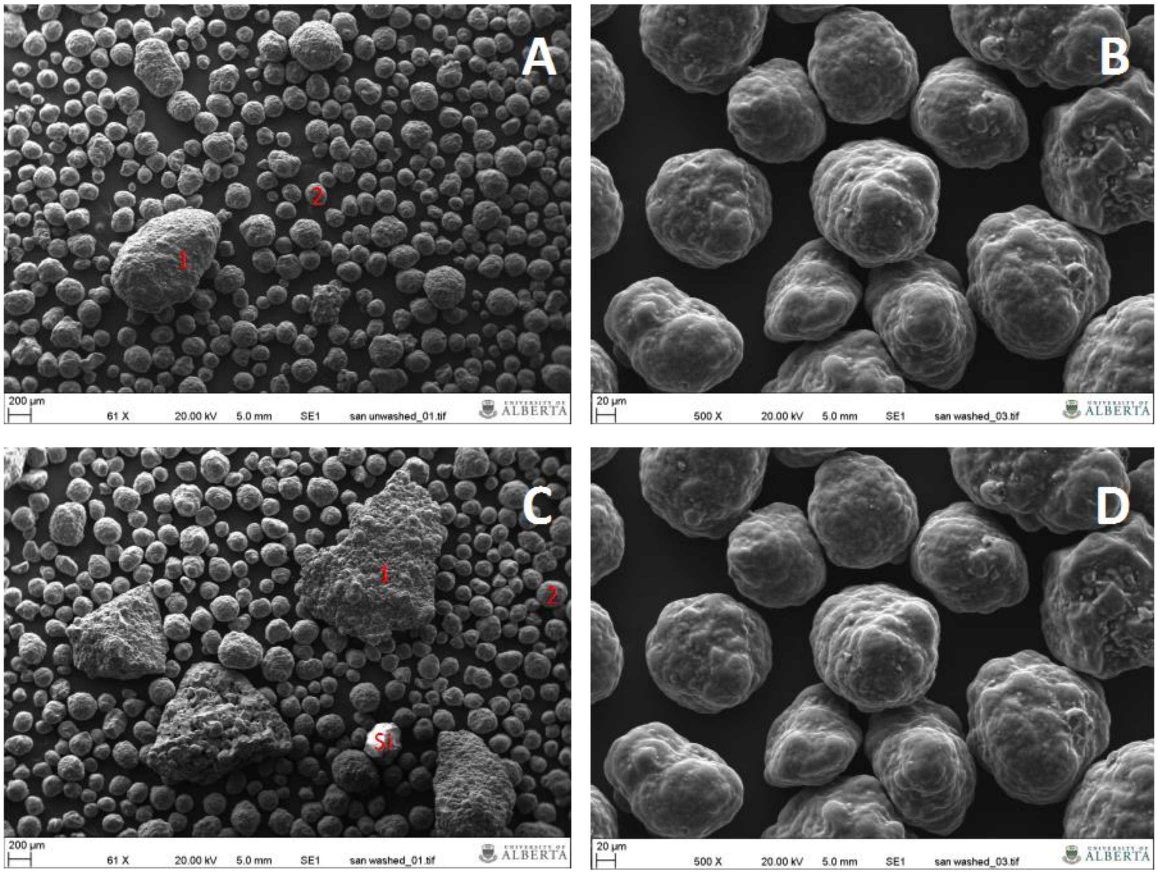


Figure 1. Scanning electron microscopy (SEM) images of Syncrude petroleum coke. (A, B) unwashed and (C, D) washed Syncrude petroleum coke (SPC). Red numbers indicate points at which energy dispersive X-ray spectroscopy (EDS) analyses for elemental composition were taken (see Appendix 2 for spectra).

Similar SEM and EDS analyses were conducted on the wheat straw (WS) biochar produced by the Alberta Biochar Initiative. At the millimetre scale, no obvious differences between the unwashed (Figure 2A) and washed (Figure 2C) biochar samples emerged. However at the micron scale, it was obvious that the washing procedure significantly impacted the surface morphology of WS. Following washing, the entire surface layer of pieces of WS is eroded, leaving behind flaky material associated with a roughened surface (Figure 2D versus 2B). It is likely that the washing procedure has increased the surface area and potentially the capacity of WS for removing contaminants from aqueous solution. Furthermore, Si nodules were observed on many WS particles (e.g., Figure 2B) and appear to have been eroded by the washing procedure (Figure 2D). EDS showed that the nodules are comprised of more than 2/3 Si and O, and that the ratio of Si:O is close to 1:2, consistent with $SiO_2(s)$ (Appendix 3). The washing procedure employed here is typically used for Boehm titrations; however, in field applications of WS and other biochars, it is unlikely that bulk volumes of the material will be washed. These Si nodules contain silanol functional groups that are proton-active and that may play some role in metal adsorption, however biochars with high fixed carbon content, and therefore hosting a high concentration of carbon-based surface functional groups, are likely to dominate metal sequestration from solution (e.g., Uchimiya et al. 2011). Element concentrations determined by EDS show that WS is comprised primarily of C, O, and Si, with smaller but considerable concentrations (> 0.1%) of K, Ca, Mg, P, S, and Al (Appendix 3). Thus while SPC has high S and relatively low Si concentrations in the solid, the composition of WS shows the opposite.

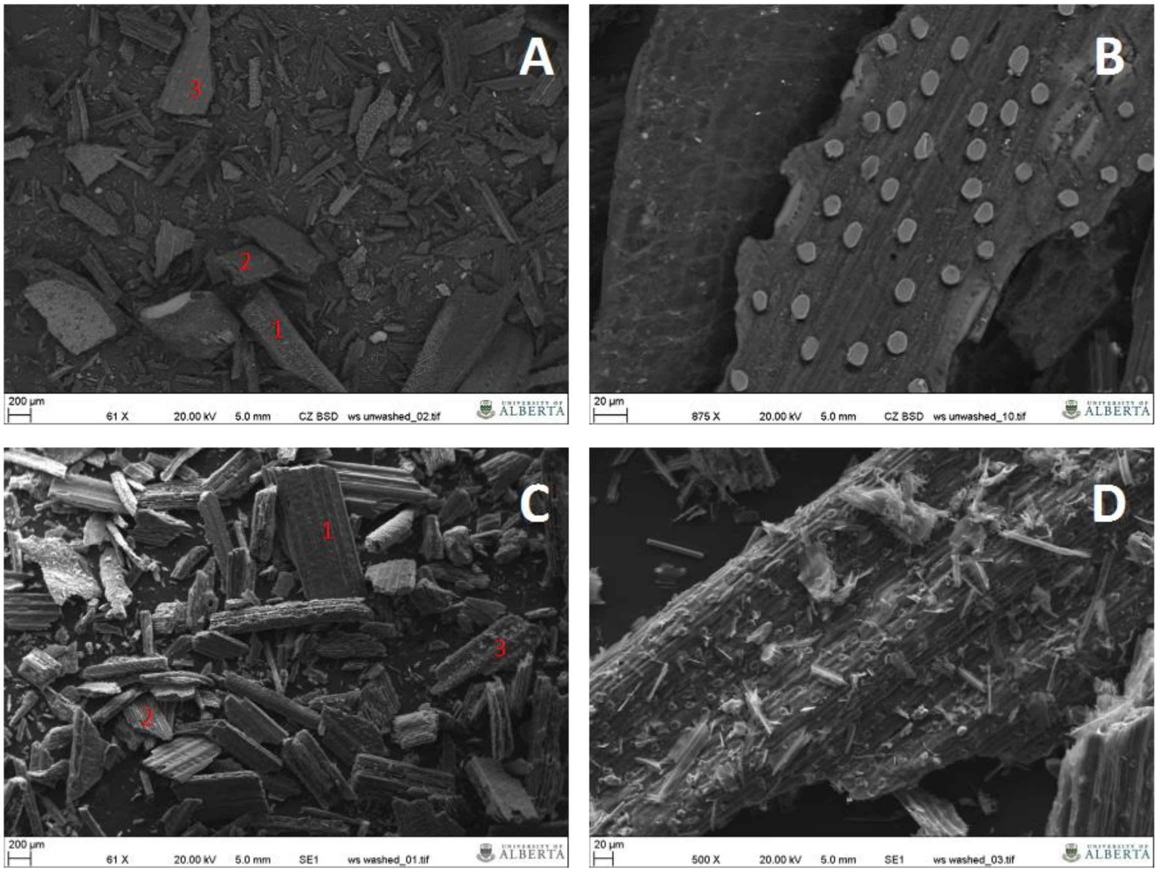
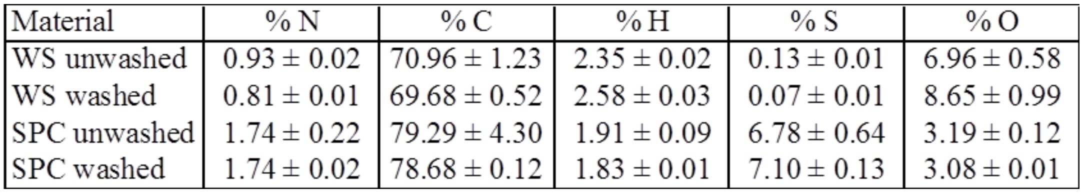


Figure 2. Scanning electron microscopy (SEM) images of willow straw biochar. (A, B) unwashed and (C, D) washed willow straw (WS) biochar. Red numbers indicate points at which energy dispersive X-ray spectroscopy (EDS) analyses for elemental composition were taken (see Appendix 3 for spectra).

3.1.2 *Major Element Analyses*

Major elements (N, C, H, S, O) in washed and unwashed samples of WS and SPC were measured (Table 1). The data are largely consistent with the SEM-EDS measurements (section 3.1.1, and Appendices 1 and 2), which show that both materials are composed primarily of C; SPC contains nearly 80% C, whereas WC contains approximately 70% C. WS contains more than twice as much oxygen as SPC, and while WS contains only traces of S, SPC contains approximately 7% S. The high content of sulphur in SPC falls in line with previous analyses of Alberta oil sands coke (Puttaswamy and Liber 2011), and is of concern when using it as a sorbent because sulfur-bearing compounds are known to leach from cokes into solution.

Table 1. Molar percentages of N, C, H, S, and O for wheat straw biochar (WS) and Syncrude petroleum coke (SPC), before and after acid washing procedure, as determined by elemental analysis.

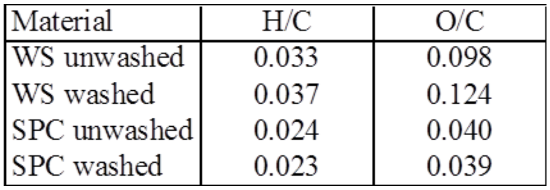


Material	% N	% C	% H	% S	% O
WS unwashed	0.93 ± 0.02	70.96 ± 1.23	2.35 ± 0.02	0.13 ± 0.01	6.96 ± 0.58
WS washed	0.81 ± 0.01	69.68 ± 0.52	2.58 ± 0.03	0.07 ± 0.01	8.65 ± 0.99
SPC unwashed	1.74 ± 0.22	79.29 ± 4.30	1.91 ± 0.09	6.78 ± 0.64	3.19 ± 0.12
SPC washed	1.74 ± 0.02	78.68 ± 0.12	1.83 ± 0.01	7.10 ± 0.13	3.08 ± 0.01

In addition, leachates from Syncrude petroleum cokes have been found to be acutely toxic to *Ceriodaphnia dubia* (Puttaswamy et al. 2010), primarily due to Ni and V release, and generally this result brings into question the suitability of SPC as a sorbent to remove naphthenic acids and metals from OSPW.

WS has higher H and O concentrations and higher H:C and O:C ratios than SPC (Table 2). Generally biochars with lower O:C ratios are considered to be more stable (Spokas 2010), and relatively lower O:C and H:C ratios are consistent with biochars produced at higher pyrolysis temperatures (Krull et al. 2009). However the sorption of dissolved organic molecules to biochar is highly dependent on the properties of the dissolved organic, and additionally may not correlate directly with biochar O:C or H:C trends, and other factors such as surface area, porosity, size of the organic molecule, or the temperature of pyrolysis (e.g., Lattao et al. 2014). There is some evidence that micro- and nano-porosity of biochar and other natural organic matter may play a large role in the uptake of dissolved organics (e.g., Han et al. 2014).

Table 2. H:C and O:C ratios of wheat straw biochar (WS) and Syncrude petroleum coke (SPC), calculated from data in Table 1.



Material	H/C	O/C
WS unwashed	0.033	0.098
WS washed	0.037	0.124
SPC unwashed	0.024	0.040
SPC washed	0.023	0.039

The most notable distinction in the WS biochar is the increase in O and H percentages following the washing procedure. This indicates that the modified Boehm titration washing procedure (Fidel et al. 2013) was removing the carbon-rich ash portion of the biochar and leaving behind larger particles with higher O and H concentrations in the resulting washed sample.

3.1.3 *Surface Area and Porosity Measurements*

Brunauer-Emmett-Teller (BET) surface area analyses show that WS has approximately five times the surface area of SPC after the washing procedure (Table 3). The Barett-Joyner-Halenda (BJH) pore size distribution analysis shows that while WS has a smaller average pore size distribution than SPC, the pore volume of WS was at least 10 times greater than that of SPC. As noted in section 3.1.2, material nanoporosity may contribute significantly to the uptake of dissolved organics from solution, and the average pore size of WS is 4 nm.

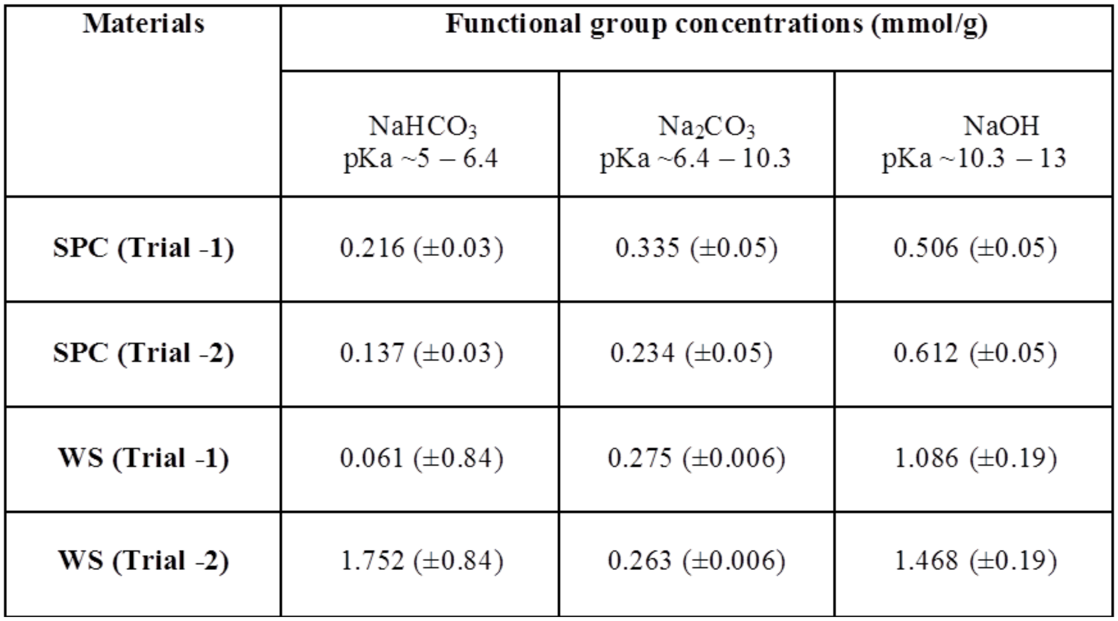
Table 3. Results of Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size distribution analyses for washed SPC and WS.

Material	BET surface area (m^2/g)	Distribution of pore size (Å)	Pore volume (cc/g)
SPC washed	5.68	38 to 42	6.2E-04
WS washed	26.64	18 to 22	5.0E-03

3.1.4 *Boehm and Potentiometric Titrations*

Boehm titrations are traditionally employed to bracket the functional group concentrations of biochars into three pKa ranges: 5 to 6.4, 6.4 to 10.3, and 10.3 to 13. We applied the method to both WS and SPC, and found that WS had a higher number of reactive sites per gram of material in all three ranges (Table 4). This result is perhaps not surprising considering the higher surface area of WS (Table 3).

Table 4. Results of Boehm titrations using the barium method for washed samples of SPC and WS.



Materials	Functional group concentrations (mmol/g)		
	$NaHCO_3$ pKa ~5 – 6.4	Na_2CO_3 pKa ~6.4 – 10.3	NaOH pKa ~10.3 – 13
SPC (Trial -1)	0.216 (±0.03)	0.335 (±0.05)	0.506 (±0.05)
SPC (Trial -2)	0.137 (±0.03)	0.234 (±0.05)	0.612 (±0.05)
WS (Trial -1)	0.061 (±0.84)	0.275 (±0.006)	1.086 (±0.19)
WS (Trial -2)	1.752 (±0.84)	0.263 (±0.006)	1.468 (±0.19)

A non-electrostatic surface complexation approach was used to model proton (H^+) adsorption data from potentiometric titrations of washed WS and SPC samples. In this model, the deprotonation of a generic functional group (A_i) on the surface of WS or SPC can be described by the following reversible reaction:

$$R - A_i - H^0 \leftrightarrow R - A_i^- + H^+ \qquad (3)$$

where R represents the SPC or WS macromolecule to which the proton active functional group A_i is attached.

The acidity constants (K_a) values are calculated according to:

$$K_{a,i} = \frac{[R - A_i^-]\, a_{H^+}}{[R - A_i - H^0]} \qquad (4)$$

where $[R–A_i^-]$ and $[R–A_i–H^0]$ represent the concentrations of the deprotonated and protonated surface functional groups, respectively, and
a_{H^+} represents the activity of protons in solution at equilibrium.

We tested 1 to 4 site models (i.e., $i = 1$ to 4), and chose the model with the lowest error as denoted by the V(Y), or variance function calculated in FITEQL 4.0 (Herbelin and Westall 1999). SPC demonstrated minimal reactivity to protons, such that the changes in solution proton concentration were not markedly different from the control experiment containing no solid and only the buffering solution. For this reason, we were not able to fit a model to the data. Because SPC is comprised of small, dense beads (Figure 1), it was not possible to get a homogeneous suspension of SPC in solution. This may have limited access of protons to SPC surface functional groups during the titrations.

Potentiometric titrations of WS biochar were successful (Table 5). The biochar exhibits proton buffering capacity across a wide range of pH, with pKa values at 3.34, 6.22, and 8.73. Site concentrations are on the order of 1 to 2E-04 mol g^{-1}, which is somewhat lower than for bacterial species (e.g., Fein et al. 1997, 2005), but significantly higher than many other sorbents in soil systems (e.g., Alessi and Fein 2010). High concentrations of proton active functional groups are important in the uptake of metals, but may not correlate directly to the ability of a biochar to remove organics from solution as compared to the porosity of the material (see section 3.1.3).

Table 5. Results of fitting of potentiometric titration data for WS biochar. Calculated variance, V(Y) was 0.86; values of $0.1 \leq V(Y) \leq 20$ are considered to be good model fits (Westall 1982).

Reactive Site	pKa	Site concentration (mol g^{-1})
1	3.34	1.175E-04
2	6.22	1.715E-04
3	8.73	2.169E-04

3.2 Model Organics Adsorption Experiments

We studied the adsorption of two model organic acids, dodecanoic acid (common name: lauric acid), and 1-methylcyclohexanecarboxylic acid (MCA), to SPC, WS, and a 1:1 mixture by mass of SPC and WS. Lauric acid is comprised of a 12-carbon saturated chain with a carboxylic acid head group (Figure 3A). MCA has similar –COOH functionality, but connected to a toluene molecule (Figure 3B). The compounds were selected to investigate differences in the adsorption of straight-chain versus cyclic organics.

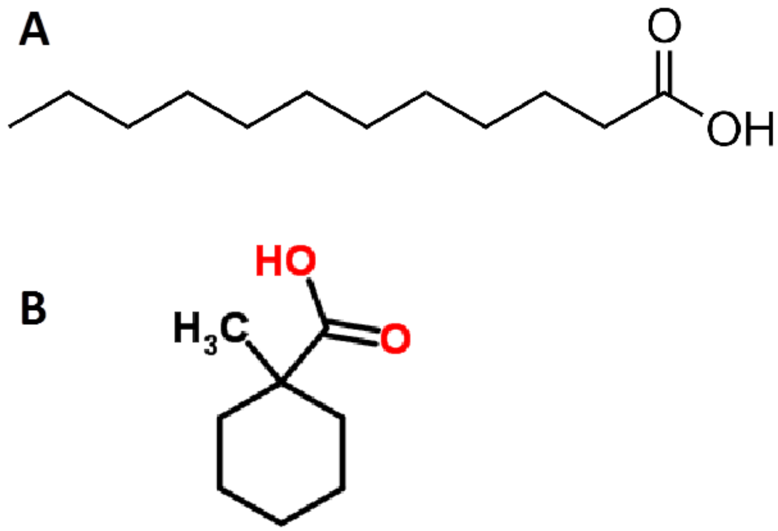


Figure 3. Skeletal formula of (A) dodecanoic (or lauric) acid (created in ChemDraw), and (B) 1-methylcyclohexanecarboxylic acid.
(from ChemSpider.com)

Figure 4 shows the results of lauric acid sorption experiments at 10 g L^{-1} solids and varying (0 to 12.5 mg L^{-1}) acid concentration. The slope of the linear equation in each panel is equivalent to the value of K_D as calculated in equations 1 and 2. Lauric acid sorption to WS biochar (Figure 4A) is approximately 5 times greater than to the SPC petroleum coke (Figure 4B). The greatest extent of lauric acid removal from solution was observed when a 1:1 admixture (by mass) of WS and SPC was used (Figure 4C). This suggests a synergy of combining the two materials, but this observation would have to be tested in experiments that are beyond the scope of this pilot study. In terms of percentage of lauric acid removal, the WS, SPC, and WS+SPC experiments removed approximately 44%, 9%, and 68% of the lauric acid in solution, respectively.

Generally our results show that MCA sorbs to both SPC and WS more weakly than lauric acid. At equivalent 10 g L^{-1} of sorbent, WS, SPC, and WS+SPC experiments removed only 18%, 2.5%, and 7% of MCA from solution, respectively (Figure 5). Murzin et al. (1997) noted that the sorption of aromatic compounds like methylcyclohexane may be limited by the size of the aromatic molecule (single benzene ring here). Once again, sorption of the organic (MCA) is stronger on WS (Figure 5A) than on SPC (Figure 5B), with K_D values of 1.8 and 0.25, respectively. However the K_D of the 1:1 mixture of WS and SPC displays a sorption capacity between the WS and SPC (Figure 5C), which is consistent with a system where the sorbents do not display synergy (i.e., where they act as a simple admixture).

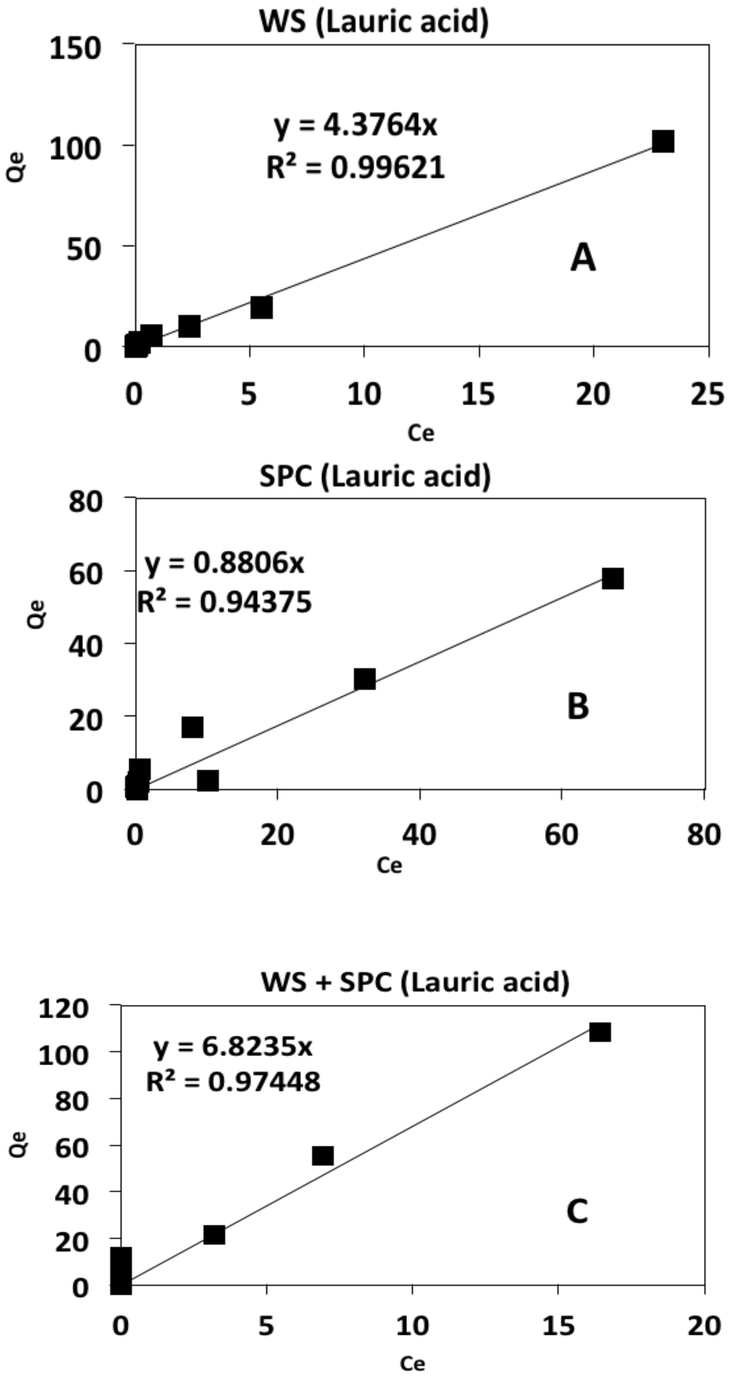


Figure 4. Adsorption data for lauric acid onto (A) WS, (B) SPC, and (C) a 1:1 mixture by mass of WS and SPC.
Solids concentration in solution is a uniform 10 g L^{-1}.
A distribution coefficient (K_D) approach is used to model the affinity of lauric acid for the solids. K_D is equivalent to the slope of the linear equation in each plot.

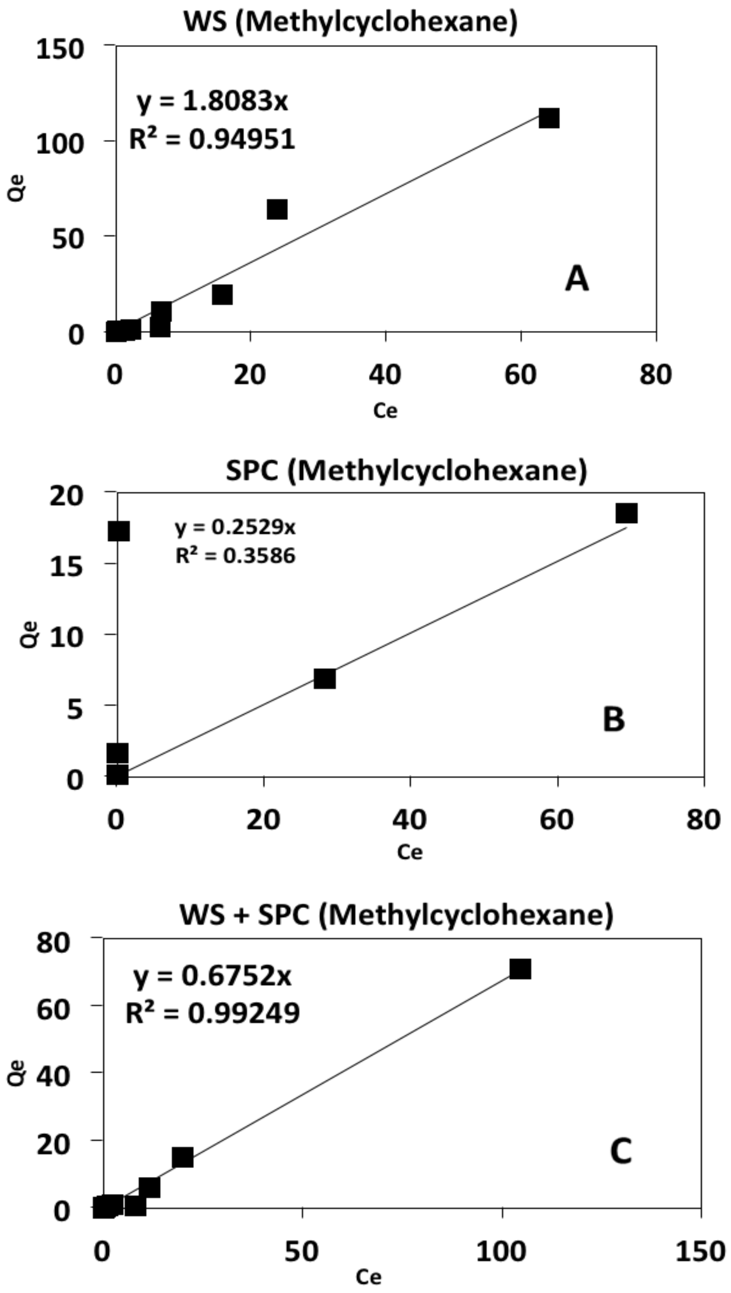


Figure 5. Adsorption data for 1-methylcyclohexanecarboxylic acid (MCA) onto (A) WS, (B) SPC, and (C) a 1:1 mixture by mass of WS and SPC.
Solids concentration in solution is a uniform 10 g L^{-1}.
A distribution coefficient (K_D) approach is used to model the affinity of MCA for the solids. K_D is equivalent to the slope of the linear equation in each plot.

4 CONCLUSIONS AND FUTURE DIRECTION

In these experiments we used batch reactors to assess the removal of MCA and lauric acid from solution by adsorption to WS, SPC, and WS+SPC. The data are fit using the linear distribution coefficient (K_D) approach, suggesting that we do not approach the sorption capacity for either sorbent. Because of the relatively low solubilities of both organic acids (*ca.* 50 mg L^{-1}; Seidell and Linke 1952), it is not possible to conduct experiments at higher acid concentrations where the sorbents may become saturated, and where modeling approaches such as the Freundlich and Langmuir isotherms could be employed. Future studies should focus on flow-through reactors, where the total sorption capacity of WS and SPC for lauric acid and MCA could be assessed.

Generally the WS biochar, produced in Alberta near the oil sands region, is a more promising sorbent for both model organic acids, although SPC removes significant organic acid from solution. If used to treat OSPW, the choice of sorbent(s) would have to be mediated by the cost of production and transport, and potential environmental concerns. For example, it is well documented that SPC contains high sulfur, and leaches metals such as V and Ni that can pose significant risks to aquatic ecosystems. Furthermore, it may be possible to regenerate biochars (and potentially petroleum cokes) loaded with naphthenic acids by heating them. Mohan et al. (2014) suggest that much more research is needed on stripping and reuse of biochars, but incineration of low-cost biochars could simultaneously produce energy and oxidize organic contaminants to carbon dioxide and water.

The organic acids tested here, lauric acid and MCA, are among the smallest molecules that might be present in OSPW. Smaller molecules in OSPW tend to be more soluble and more toxic, and present the highest risk to aquatic ecosystems (Frank et al. 2008). Because of their relatively low molecular weight and higher solubility, the extent of lauric acid and MCA sorption to WS and SPC is likely lower than for most organic acids that are found in OSPW. Larger organic molecules, or a test of naphthenic acids removal from OSPW, should be conducted to further validate the field efficiency of the sorbents.

Mixtures of biochar and petroleum coke could be promising for a second reason. Biochars are generally good sorbents for removing metals from solution (Ahmad et al. 2013b). In this study, we conducted one of the first potentiometric titration experiments of a biochar, and showed that WS has significant proton buffering capacity across a wide range of pH. If SPC is used as a sorbent for organic acids in OSPW, and it releases metals of environmental concern into the processed waste stream, biochar may be used as a secondary treatment or in a mixture of SPC and WS to remove these metals before the water is released. This conjecture would require experiments to test. However, if the cost of WS is less than or comparable to using SPC, then using the biochar itself will be more effective at removing the model organic compounds tested here from solution.

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6 GLOSSARY

6.1 Terms

Adsorption

The removal of ions, molecules, or atoms from aqueous solution by attachment to a solid surface.

Biochar

Biomass pyrolyzed in a low or no oxygen environment.

Coke

Carbon rich waste created as a byproduct of the cracking process during the processing of petroleum hydrocarbons.

Deprotonation

The removal of a hydrogen ion (H^+; or proton) from a functional group on a solid surface or a molecule in solution.

Equilibrium Sorption Capacity

A term (q_e) in the Langmuir adsorption isotherm that defines the theoretical maximum capacity of a sorbent to remove an ion, atom, or molecule from solution.

pKa

The negative log of the acid dissociation constant (K_a), which is a measure of the capacity for a particular functional group to react with protons (H^+) in solution.

Pore Volume

The quotient of the amount of void space in a unit of a solid divided by the total volume of the same unit of solid.

Pore Diameter

The distance across the openings in a porous medium such as biochar or petroleum coke.

Potentiometric Titration

A technique used to quantify the proton (H^+) reactivity of the surfaces of a solid (e.g., biochar, petroleum coke) or a molecule in solution.

Sorptive Capacity

The measured maximum capacity of a sorbent to remove an atom, ion, or molecule from solution.

Specific Surface Area

The total surface area of a solid per unit mass.

6.2 Acronyms

ABI	Alberta Biochar Initiative
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
EDS	Energy Dispersive X-Ray Spectroscopy
HPLC-MS	High Performance Liquid Chromatography – Mass Spectrometry
OSPW	Oil Sands Process-Affected Water
OSRIN	Oil Sands Research and Information Network
SEE	School of Energy and the Environment
SEM	Scanning Electron Microscopy

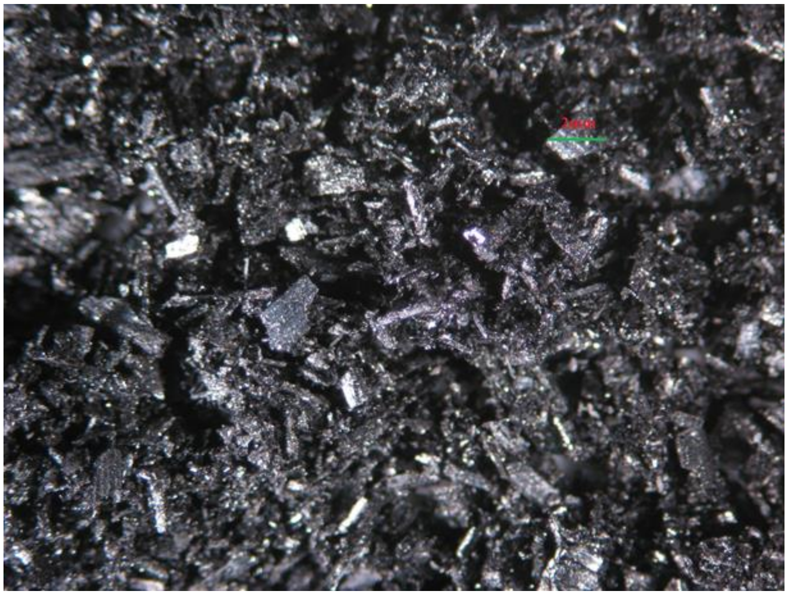
6.3 Chemicals

$BaCl_2$	Barium chloride
$CaCl_2$	Calcium chloride
HCl	Hydrochloric acid
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate
OA	Organic Acids
LA	Lauric Acid
MCA	1-Methylcyclohexanecarboxylic acid

APPENDIX 1: Light Microscopy Images.

Light microscopy images of (A) wheat straw (WS) biochar produced by the Alberta Biochar Initiative, and (B) Syncrude petroleum coke (SPC).

A



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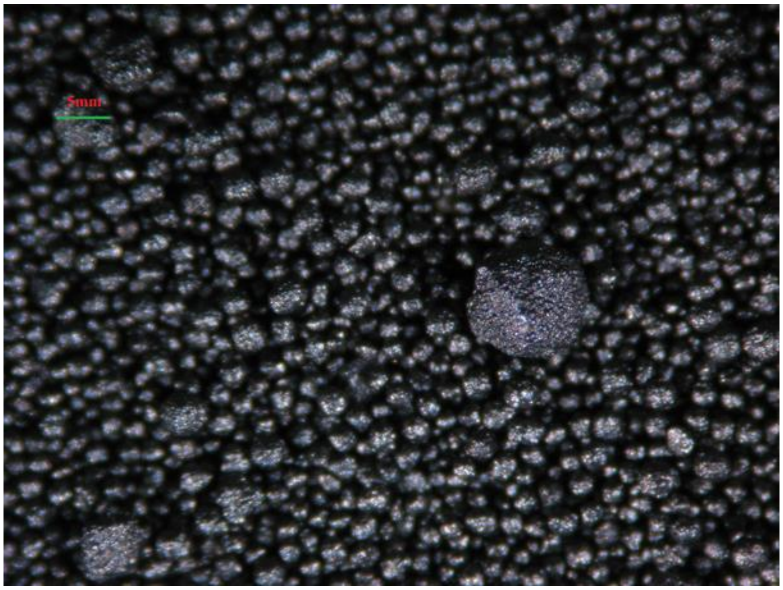
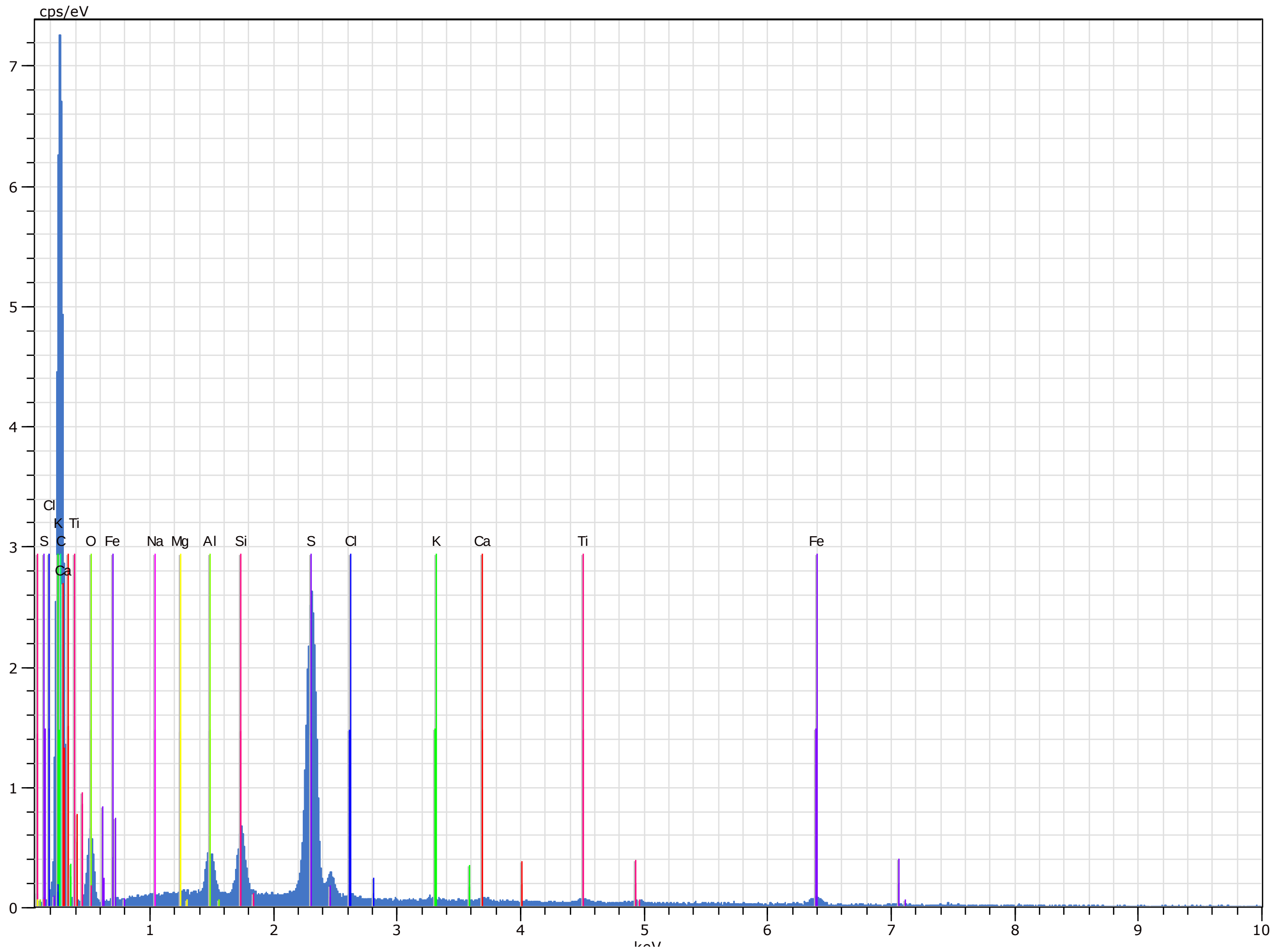


APPENDIX 2: Energy Dispersive X-ray Spectroscopy (EDS) Data for Syncrude Petroleum Coke (SPC).

Energy dispersive X-ray spectroscopy (EDS) measurements of elemental composition were taken while collecting the scanning electron microscopy (SEM) images. Data from several points on each of the four solids were collected: wheat straw (washed), wheat straw (unwashed), petroleum coke (washed), and petroleum coke (unwashed). Vertical lines in each diagram indicate the K-edge energy (in units of keV) at which a particular elemental peak should appear in the accompanying spectral measurement. The element corresponding to a position is indicated at the top of each vertical line. Following each spectrum is an explanation of the sample analyzed, and a table indicating the percent each element contributes to the total composition of the solid.

It should be noted that EDS data are semi-quantitative at best; however, as discussed in the main report text, the correlation between the EDS data and independent chemical digestions of the biochar and petroleum coke samples is strong.



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C  6  K-series  76.51   75.34   83.73         9.24
O  8  K-series  14.64   14.41   12.02         2.33
S  16 K-series   6.88    6.77    2.82         0.28
Si 14 K-series   1.10    1.08    0.51         0.08
Al 13 K-series   0.90    0.89    0.44         0.07
Fe 26 K-series   0.72    0.71    0.17         0.06
Ti 22 K-series   0.28    0.27    0.08         0.04
Ca 20 K-series   0.12    0.12    0.04         0.03
K  19 K-series   0.12    0.12    0.04         0.03
Na 11 K-series   0.11    0.11    0.06         0.04
Cl 17 K-series   0.11    0.10    0.04         0.03
Mg 12 K-series   0.08    0.07    0.04         0.03
-----------------------------------------------------
       Total: 101.55  100.00  100.00
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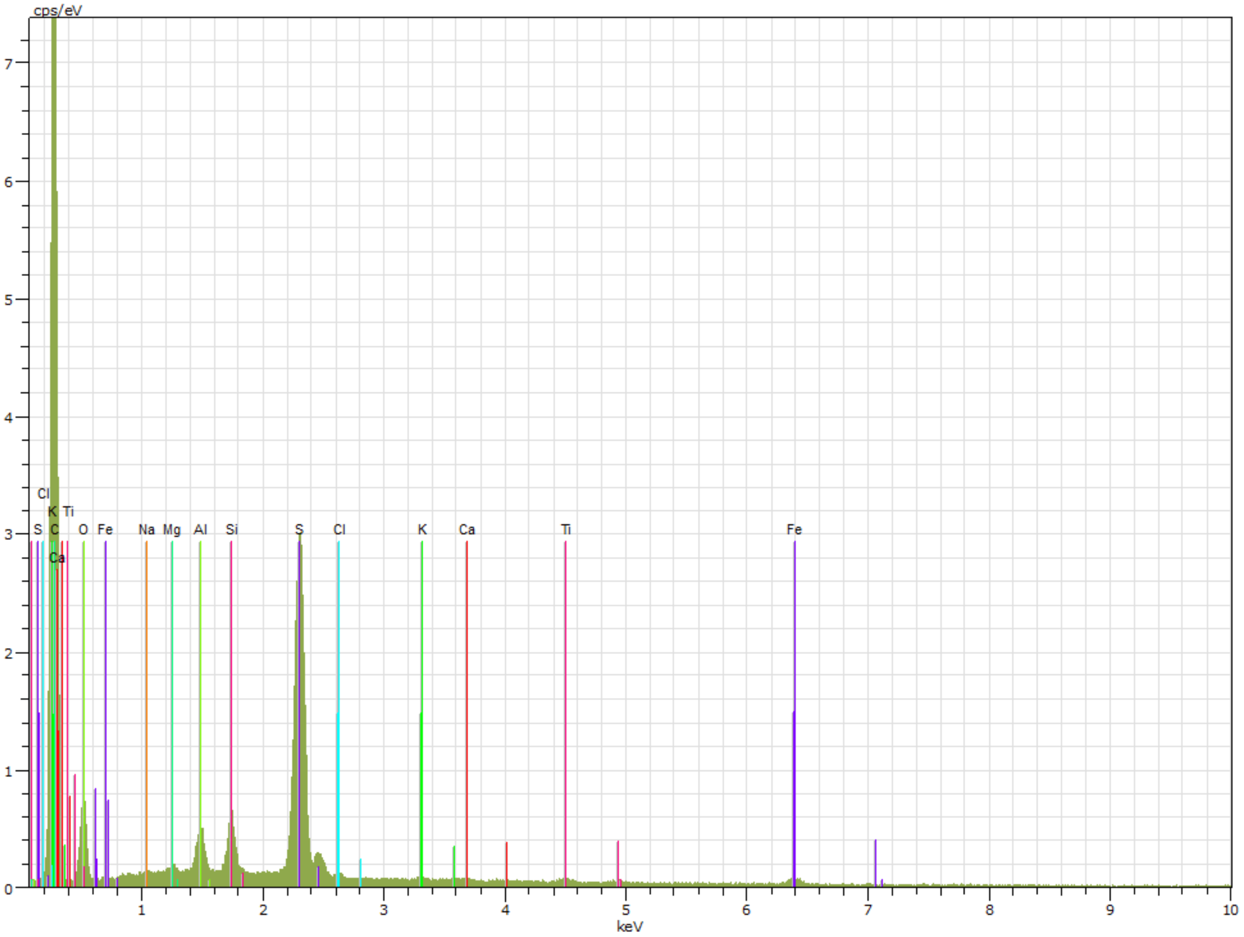

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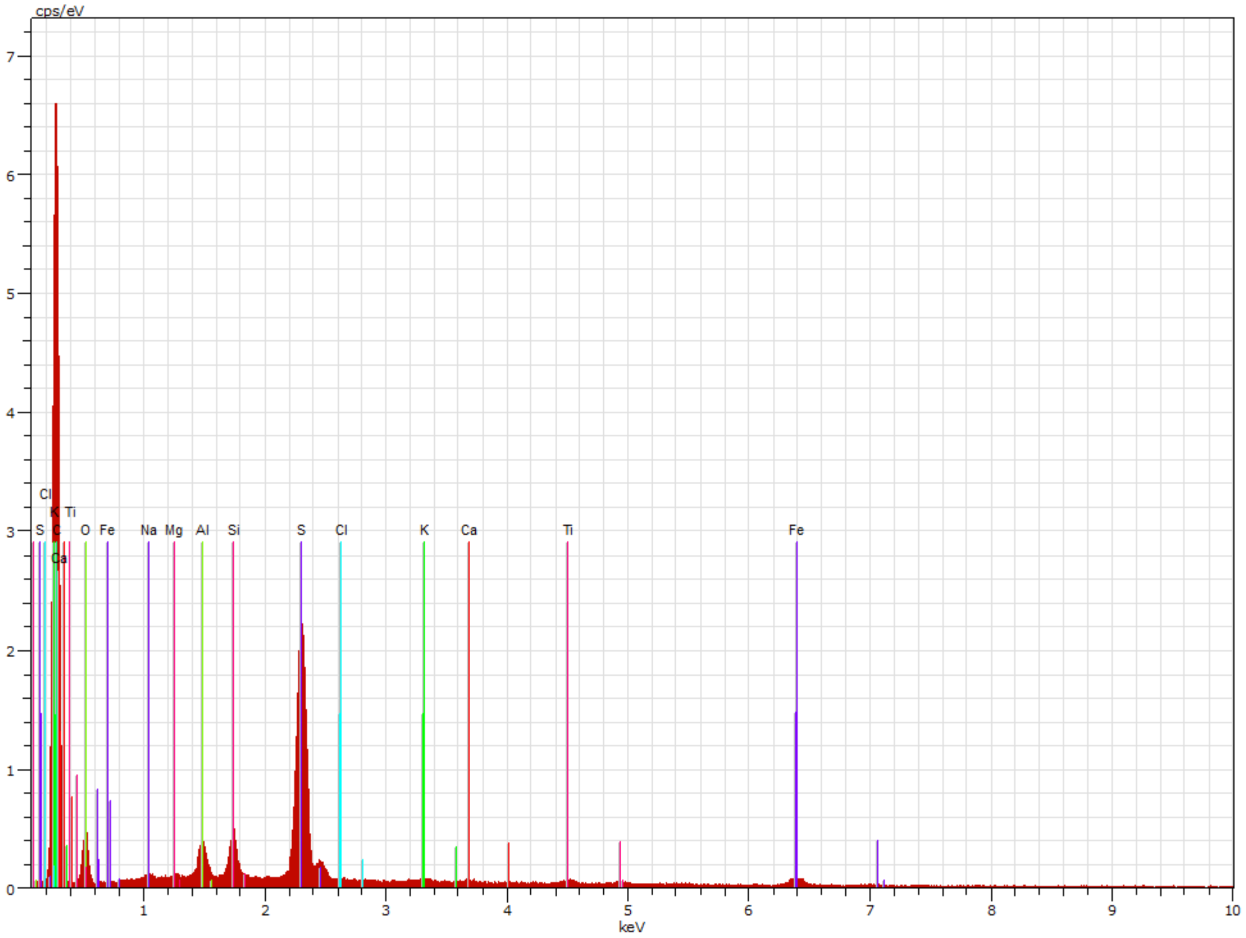
O	8	K-series	15.07	15.07	12.55	2.26
S	16	K-series	6.54	6.54	2.72	0.26
Si	14	K-series	0.94	0.94	0.44	0.07
Al	13	K-series	0.83	0.83	0.41	0.07
Fe	26	K-series	0.61	0.61	0.15	0.05
Ti	22	K-series	0.25	0.25	0.07	0.04
Na	11	K-series	0.14	0.14	0.08	0.04



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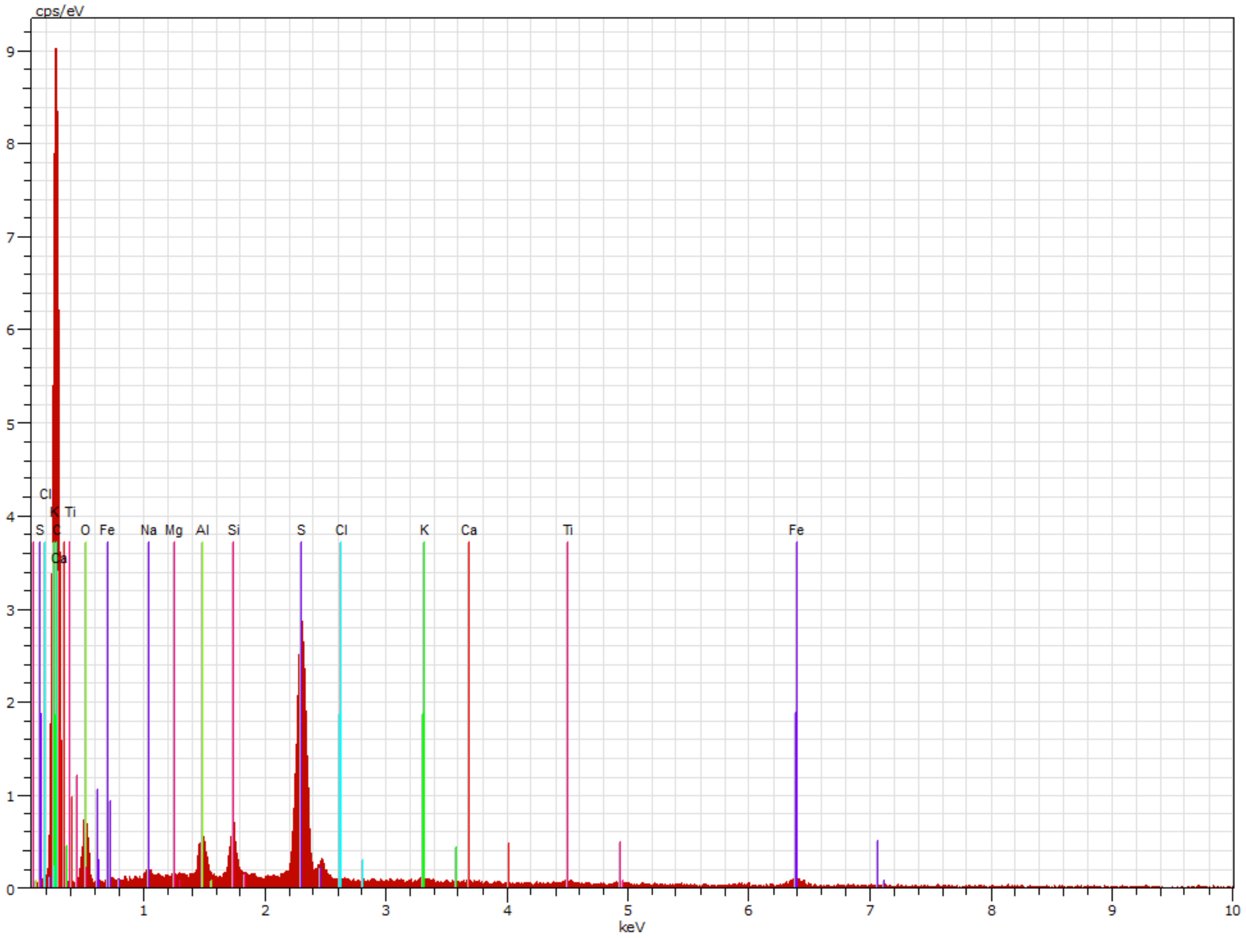
-----------------------------------------------------
C  6  K-series  77.46   77.10   85.43         9.09
O  8  K-series  12.37   12.32   10.24         1.93
S  16 K-series   6.61    6.57    2.73         0.26
Fe 26 K-series   1.07    1.06    0.25          0.06
Si 14 K-series   1.01    1.00    0.47         0.07
Al 13 K-series   0.91    0.90    0.44          0.07
Ti 22 K-series   0.35    0.35    0.10          0.04
Na 11 K-series   0.27    0.27    0.16          0.05
```



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-----------------------------------------------------
C  6  K-series  75.49   75.49   83.59         9.72
O  8  K-series  15.06   15.06   12.51         2.75
S  16 K-series   6.26    6.26    2.60         0.26
Fe 26 K-series   0.88    0.88    0.21          0.07
Si 14 K-series   0.85    0.85    0.40          0.07
Al 13 K-series   0.79    0.79    0.39          0.07
Na 11 K-series   0.29    0.29    0.17          0.06
Ti 22 K-series   0.20    0.20    0.06          0.04
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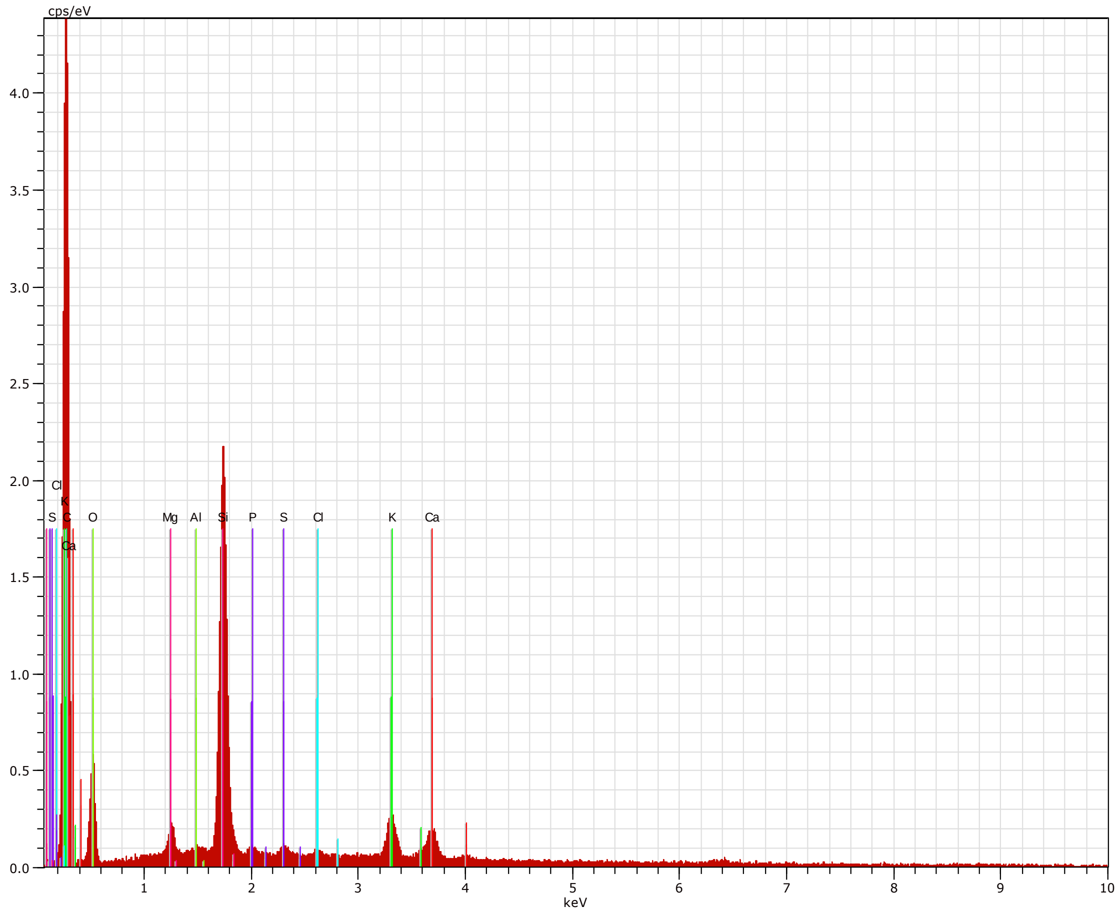
APPENDIX 3: Energy Dispersive X-ray Spectroscopy (EDS) Data for Wheat Straw (WS) Biochar.



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-----------------------------------------------------
C  6  K-series  56.24   69.08   78.37           7.33
O  8  K-series  15.43   18.95   16.14           2.69
Si 14 K-series   6.42    7.88    3.82           0.31
K  19 K-series   1.08    1.32    0.46           0.07
Ca 20 K-series   1.00    1.23    0.42           0.07
Mg 12 K-series   0.72    0.88    0.49           0.08
P  15 K-series   0.17    0.21    0.09           0.04
S  16 K-series   0.17    0.21    0.09           0.04
Al 13 K-series   0.11    0.13    0.07           0.04
Cl 17 K-series   0.09    0.11    0.04           0.03
-----------------------------------------------------
       Total:  81.41  100.00  100.00
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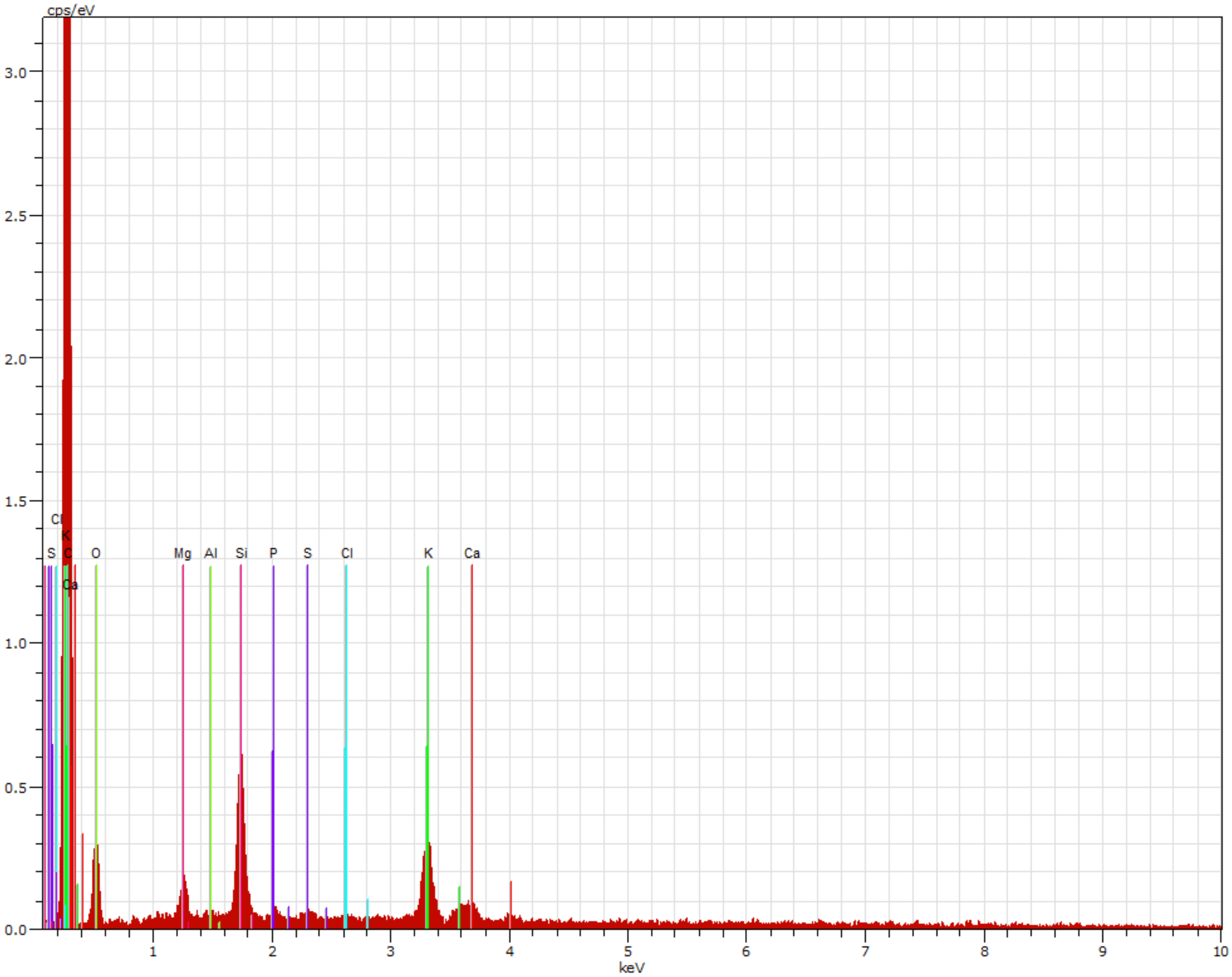

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-----------------------------------------------------
C  6  K-series  75.38   75.38   82.80           10.13
O  8  K-series  17.06   17.06   14.07            3.64
Si 14 K-series   2.98     2.98    1.40           0.17
K  19 K-series   2.79     2.79    0.94           0.13
Mg 12 K-series   0.82     0.82    0.45            0.09
Ca 20 K-series   0.67     0.67    0.22           0.06
S  16 K-series   0.15     0.15    0.06           0.04
```

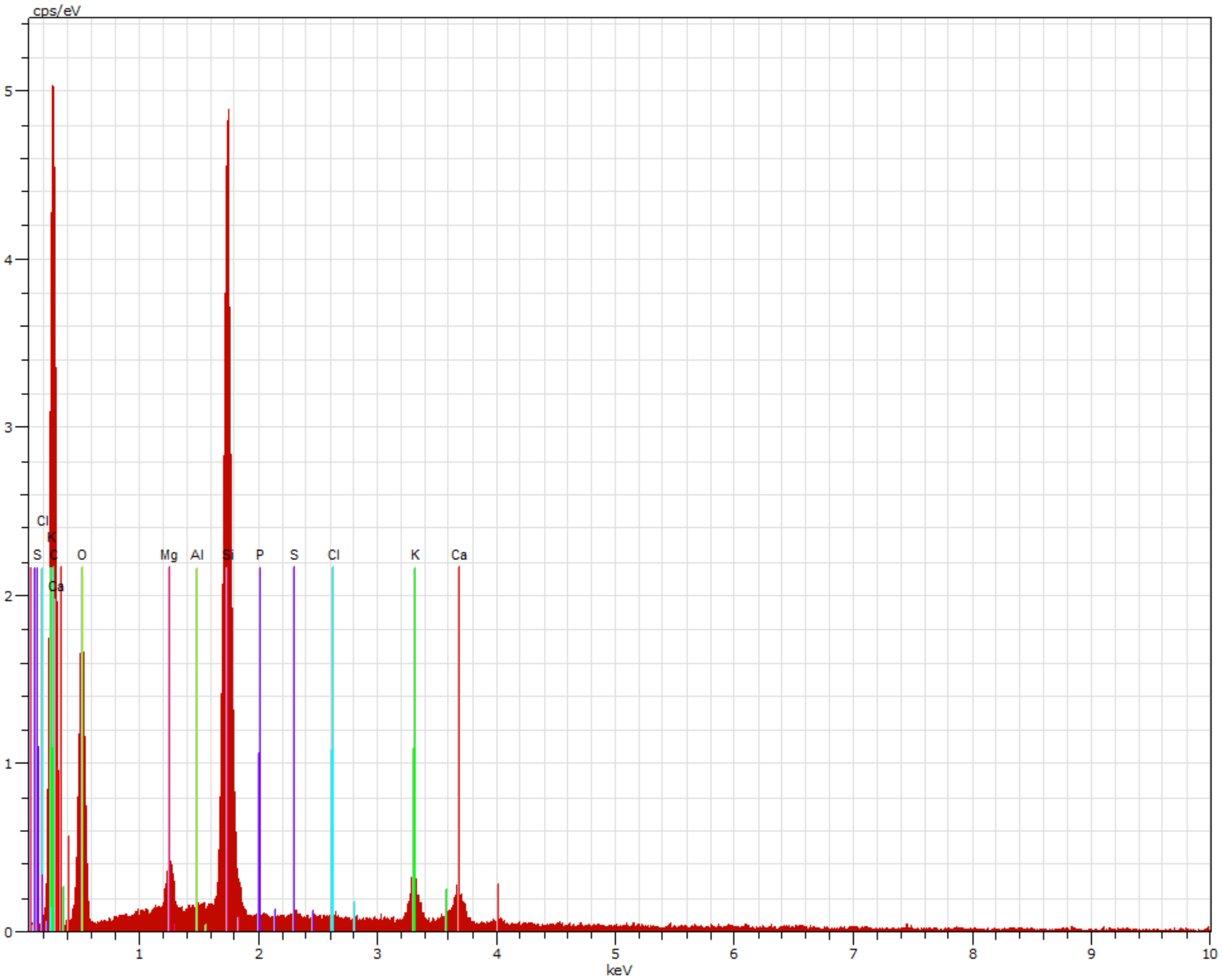

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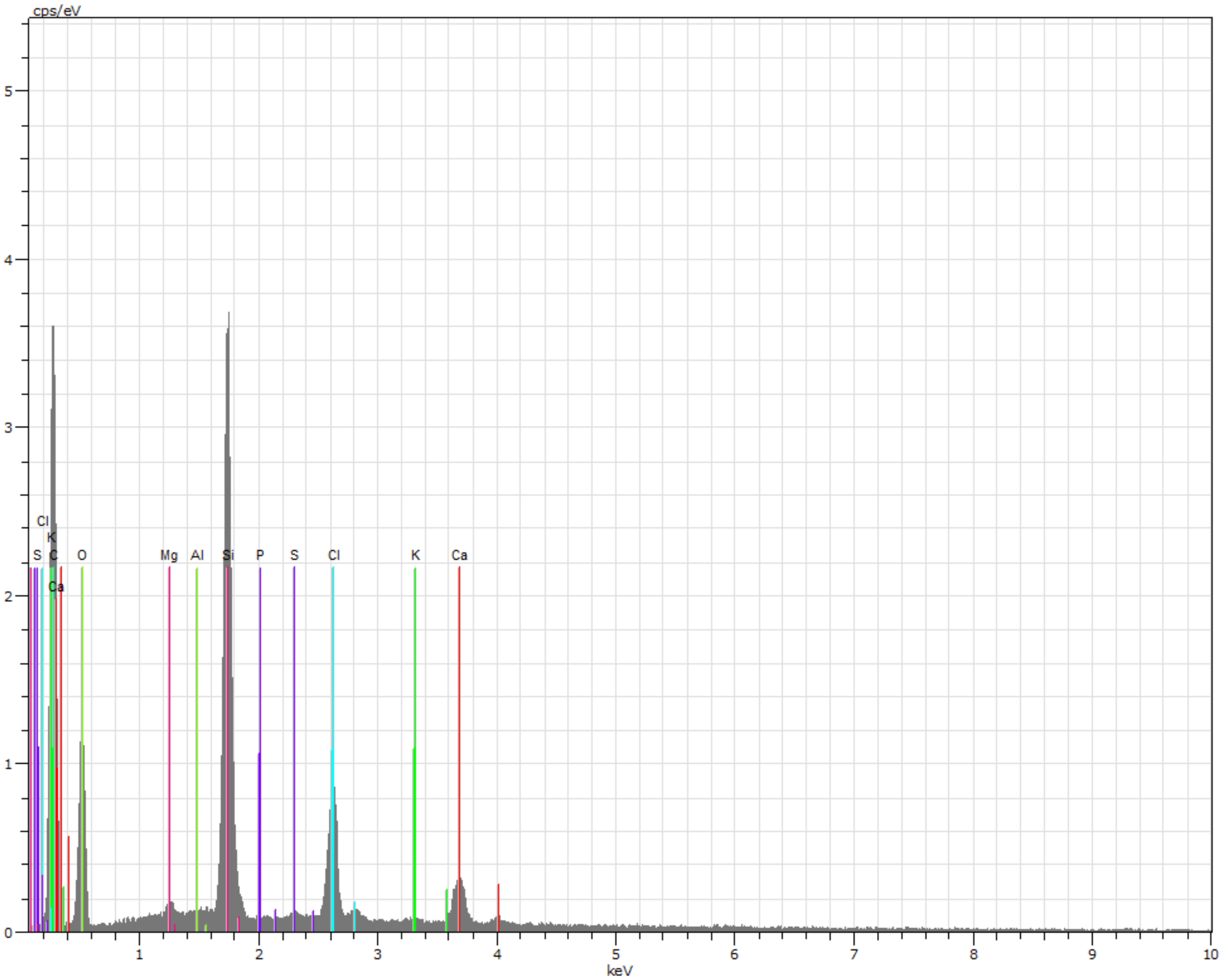
C	6	K-series	47.32	54.95	65.45	6.21
O	8	K-series	26.68	30.99	27.70	3.83
Si	14	K-series	9.04	10.49	5.35	0.42
Ca	20	K-series	1.12	1.30	0.46	0.07
K	19	K-series	0.97	1.13	0.41	0.06
Mg	12	K-series	0.71	0.82	0.49	0.07
Cl	17	K-series	0.12	0.14	0.06	0.03



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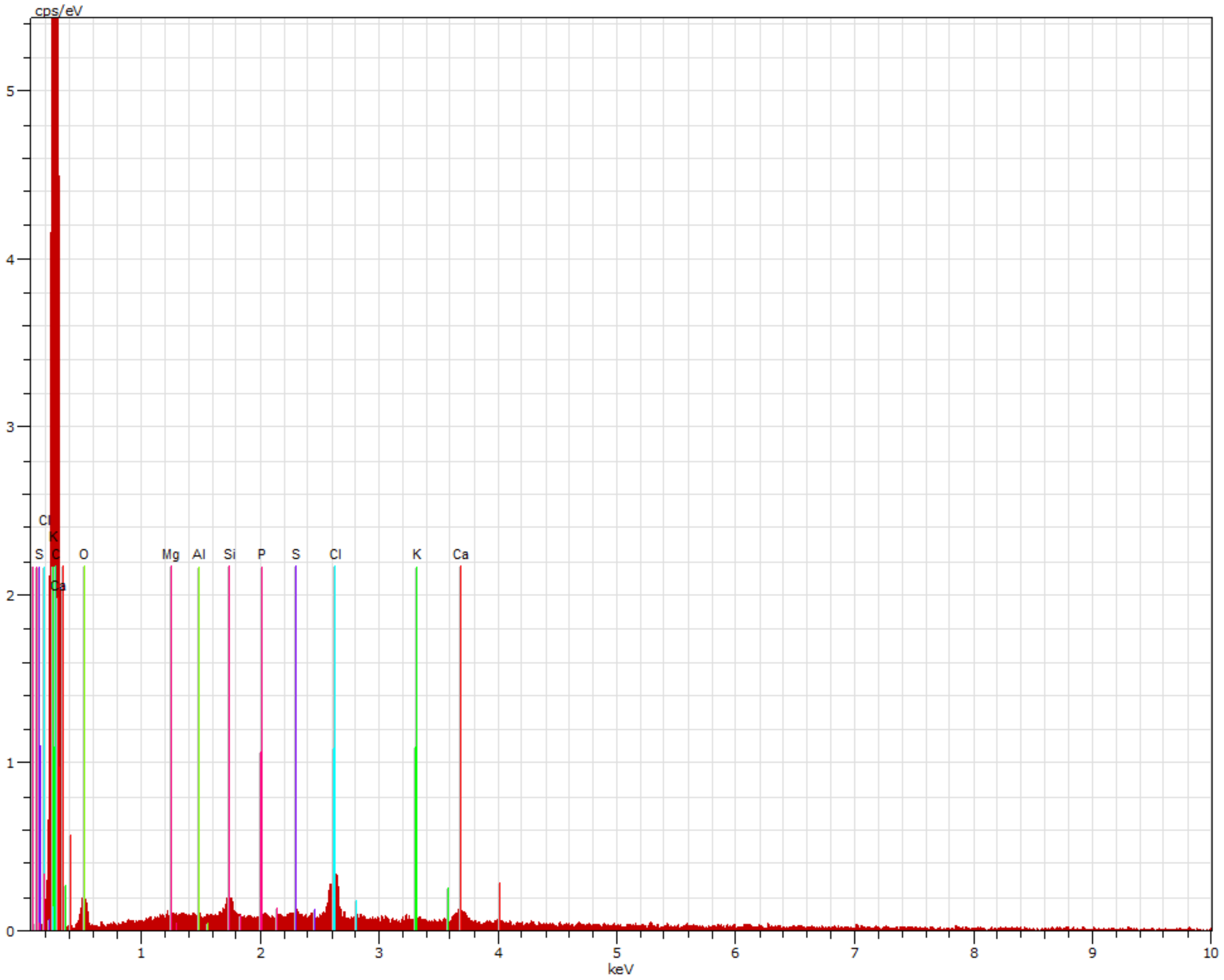
C	6	K-series	48.00	56.33	67.56	6.19
O	8	K-series	23.62	27.72	24.96	3.34
Si	14	K-series	8.30	9.74	5.00	0.38
Cl	17	K-series	2.86	3.35	1.36	0.13
Ca	20	K-series	1.86	2.18	0.78	0.09
Mg	12	K-series	0.26	0.31	0.18	0.04
K	19	K-series	0.14	0.16	0.06	0.03



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-----------------------------------------------------
C  6  K-series  89.63   89.63   92.91          10.90
O  8  K-series   7.97    7.97    6.20           1.87
Cl 17 K-series   1.04    1.04    0.36           0.07
Ca 20 K-series   0.59    0.59    0.18           0.06
Si 14 K-series   0.36    0.36    0.16           0.05
Mg 12 K-series   0.17    0.17    0.09           0.04
K  19 K-series   0.12    0.12    0.04           0.04
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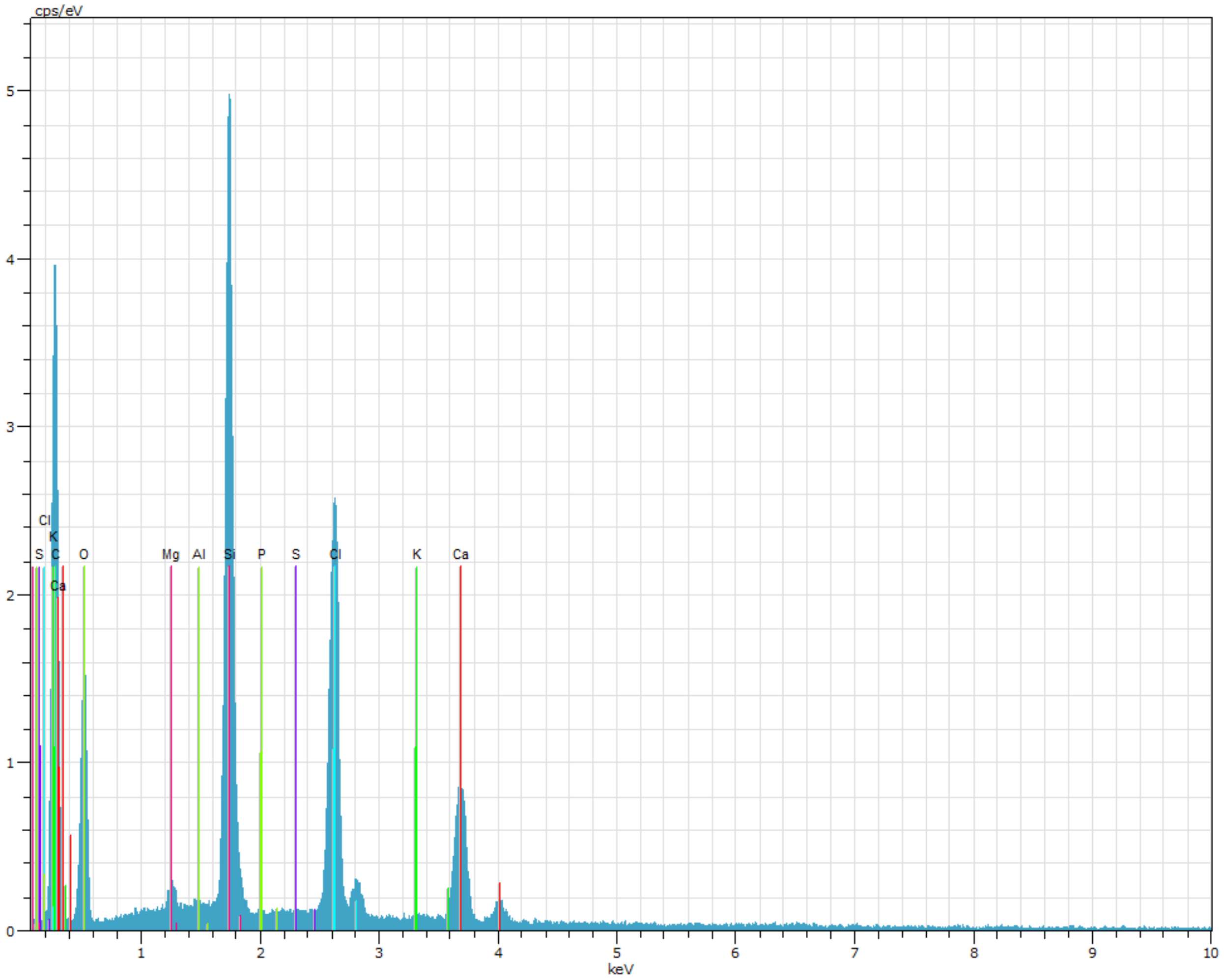

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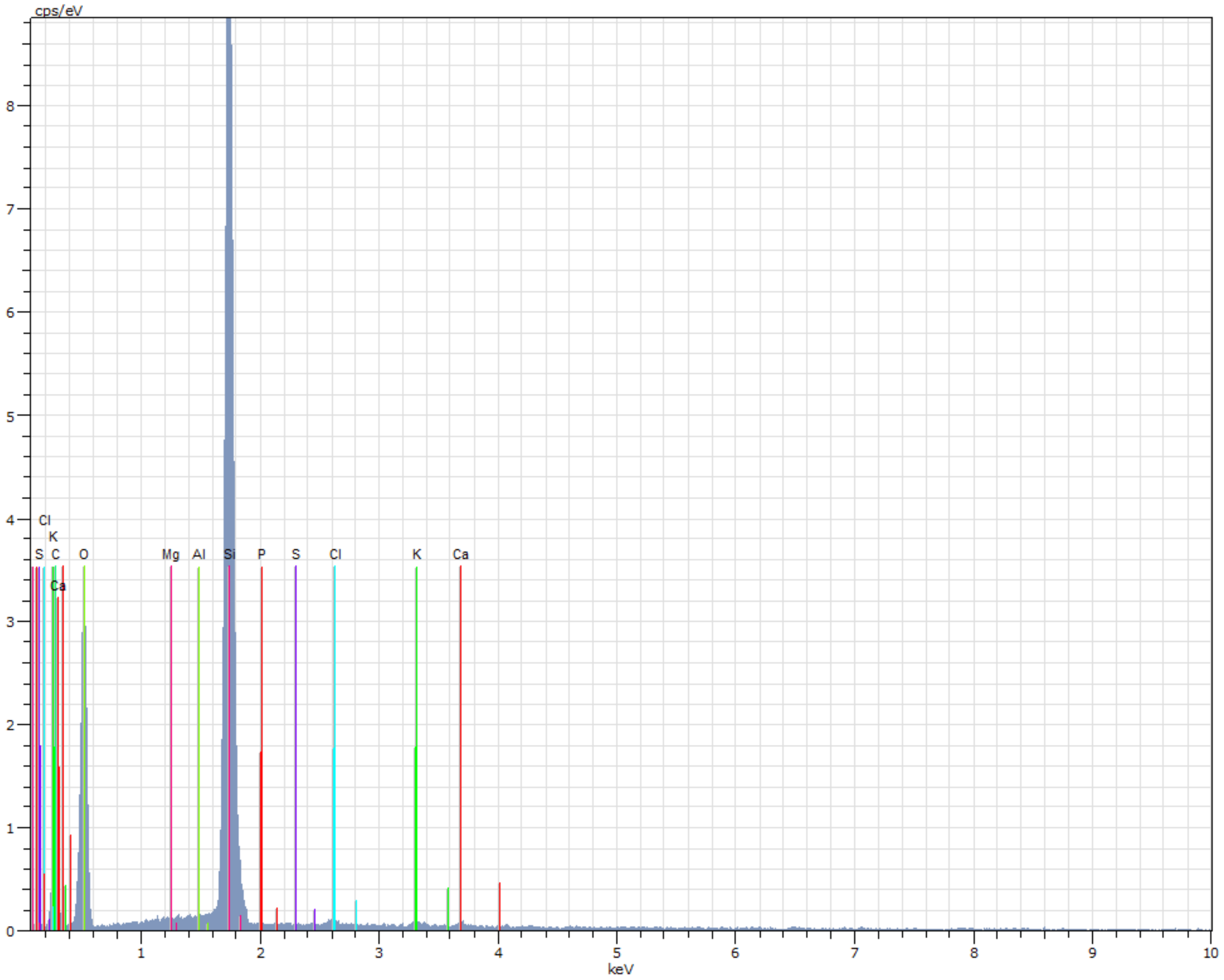
-----------------------------------------------------
C  6  K-series  57.59   52.69   65.81            7.75
O  8  K-series  28.35   25.94   24.32            4.13
Si 14 K-series   9.43    8.63    4.61            0.43
Cl 17 K-series   8.19    7.49    3.17            0.31
Ca 20 K-series   5.03    4.60    1.72            0.18
Mg 12 K-series   0.43    0.39    0.24            0.06
K  19 K-series   0.13    0.12    0.05            0.03
```



ws washed_ 4 Date:7/8/2014 11:05:15 AM HV:20.0kV Puls th.:1.78kcps

```
El AN  Series  unn. C norm. C Atom. C Error (1 Sigma)
               [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------
O  8  K-series  43.66   44.21   47.95            5.83
Si 14 K-series  32.84   33.25   20.55            1.43
C  6  K-series  21.14   21.40   30.92            3.84
Cl 17 K-series   0.32    0.33    0.16            0.05
Ca 20 K-series   0.29    0.29    0.13            0.05
K  19 K-series   0.22    0.23    0.10            0.04
Al 13 K-series   0.18    0.19    0.12            0.04
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