Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Hydrothermal metal recovery of metal-contaminated wastewater with forest residue: A zero waste discharge process

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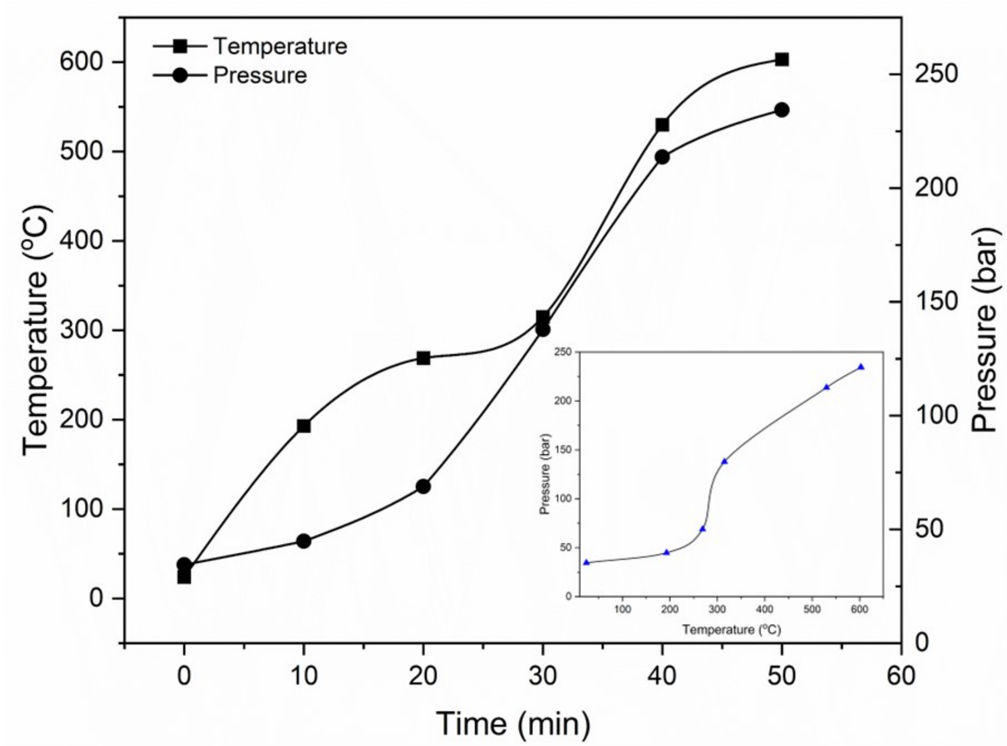

Fig. S1 Pressure and temperature profile w.r.t time in the reactor

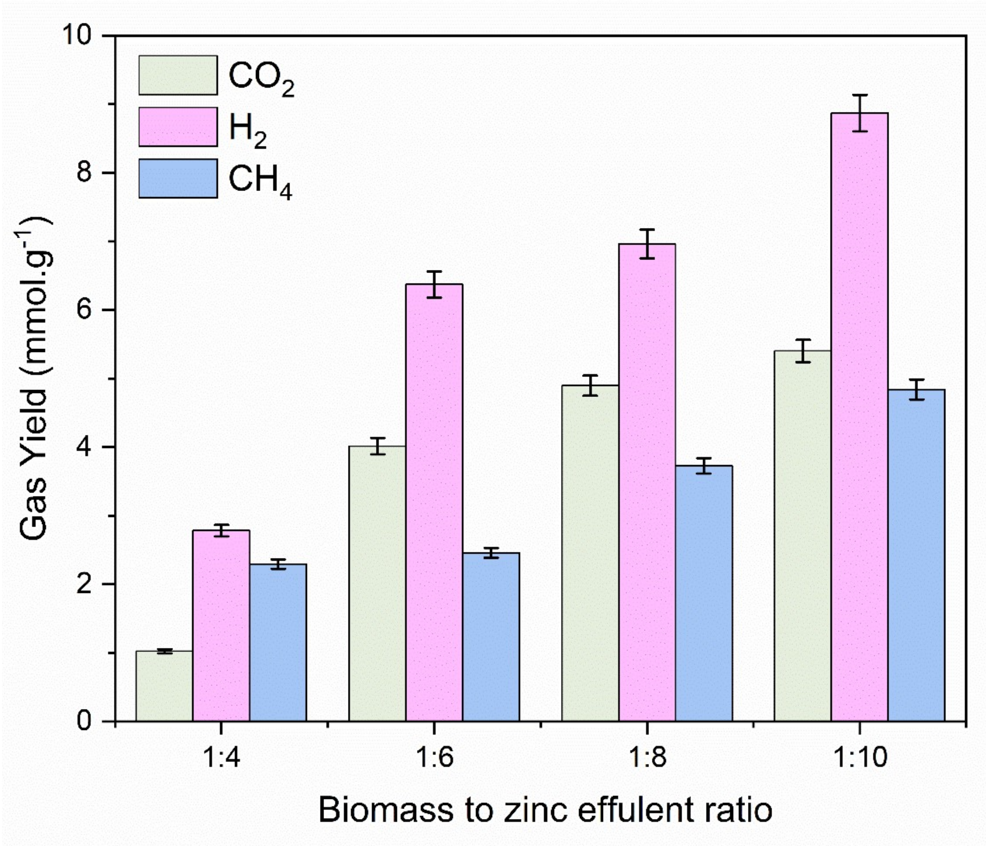

Fig. S2 Effect of feed concentration on gasification performance of simulated zinc metal effluent with pine needles at 600 C, B:SME::1:10 and 60 min.

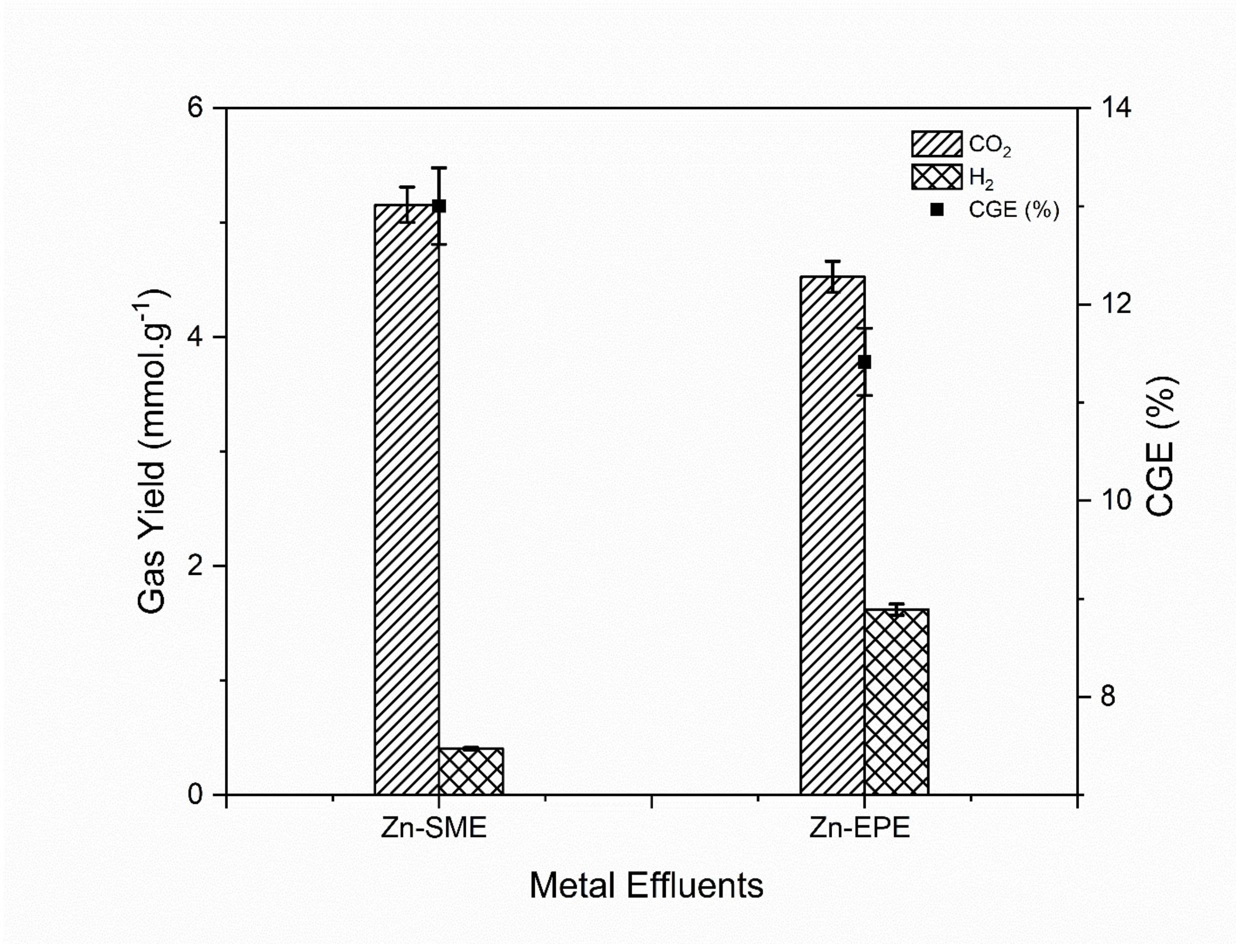

Fig. S3 Gasification performance of simulated zinc metal effluent (Zn-SME) and real electroplating metal effluent (Zn-EPE) with pine needles at 400 ^{o}C, 30 min, and biomass to metal effluent ratio 1:100.

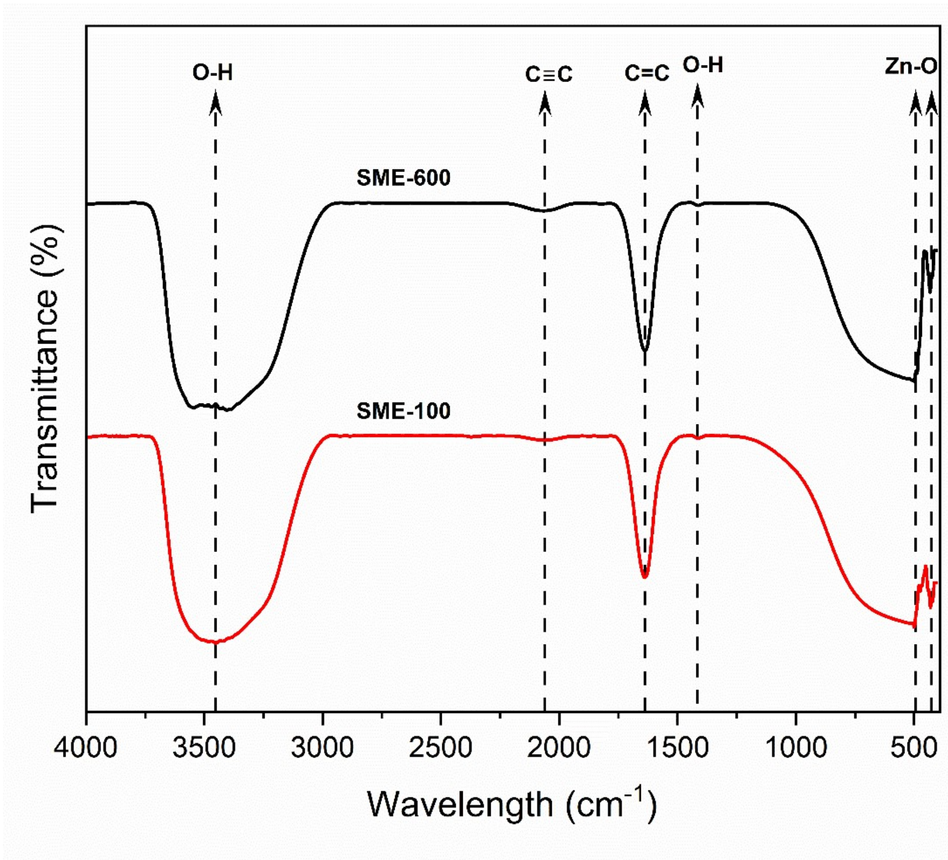

Fig. S4 FTIR spectra of the treated aqueous phase were obtained at 100 °C and 600 °C, 60 min residence time, and B: SME:1:10.

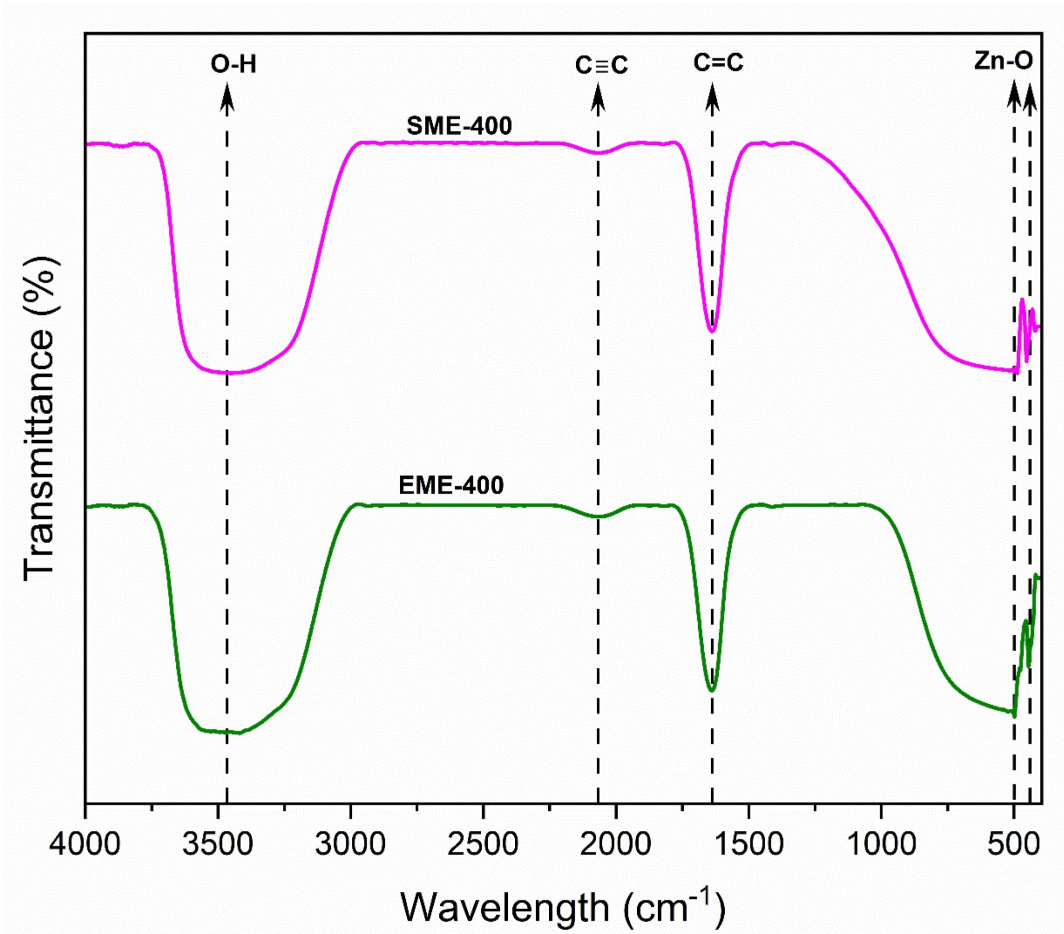

Fig. S5 FTIR spectra of the treated aqueous phase were obtained at 400 ^{o}C, 30 min residence time, and B: SME:1:100.

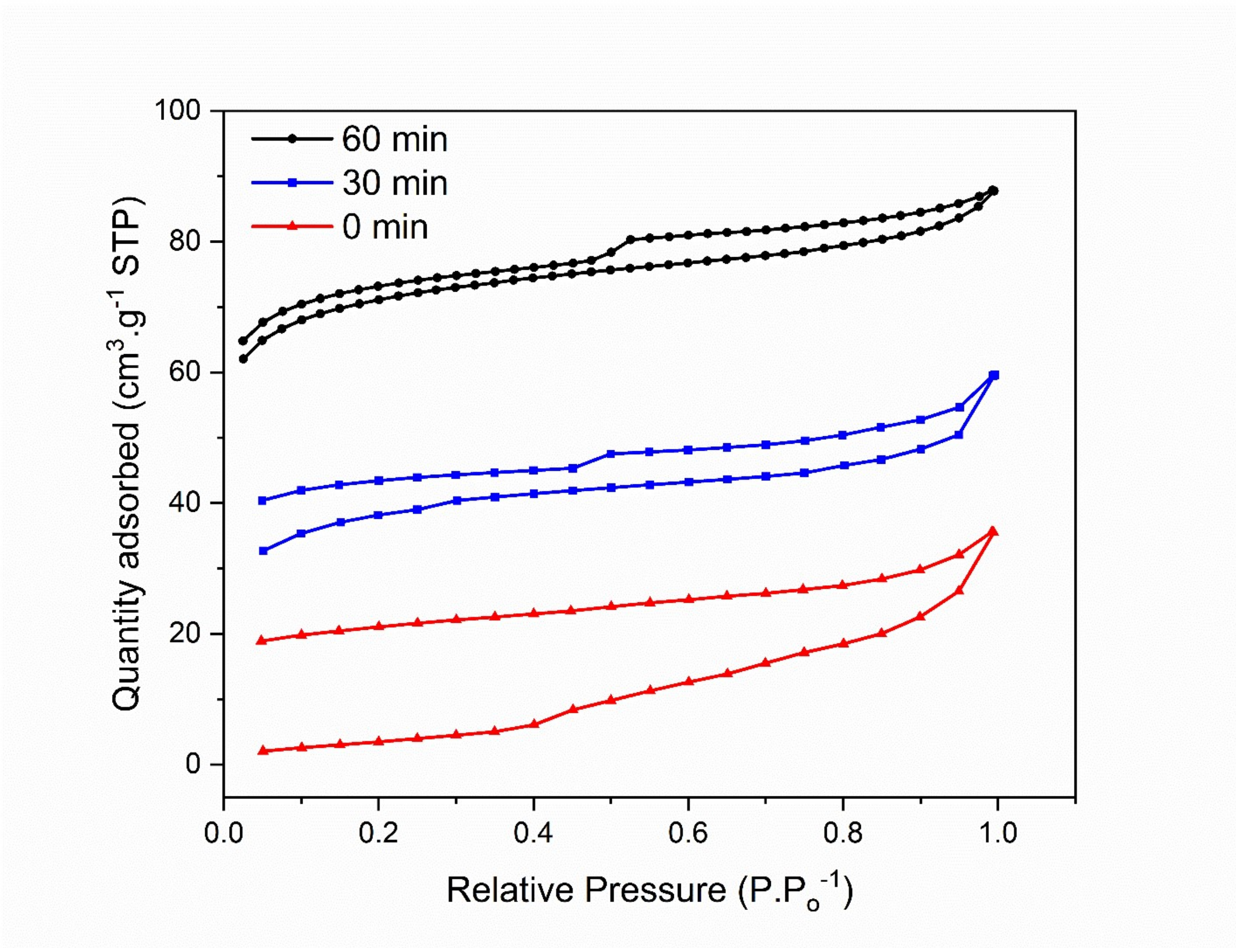

Fig. S6 Nitrogen adsorption-desorption isotherm of carbon composite obtained at 0 min, 30 min and 60 min at 600 ^{o}C and biomass to effluent ratio 1:10.

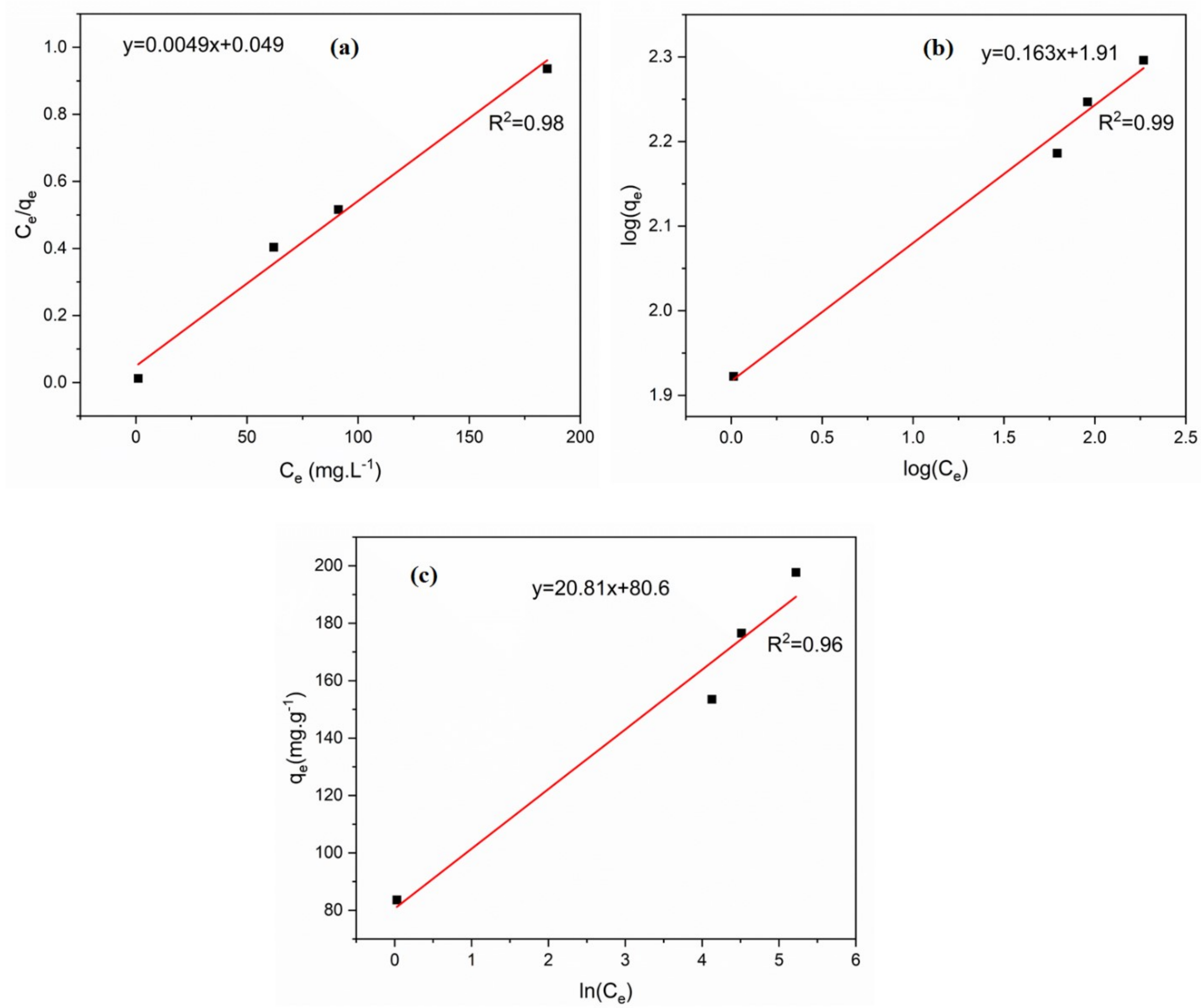

Fig. S7 Isotherm fitting of (a) Langmuir (b) Freundlich and (c) Temkin Models.

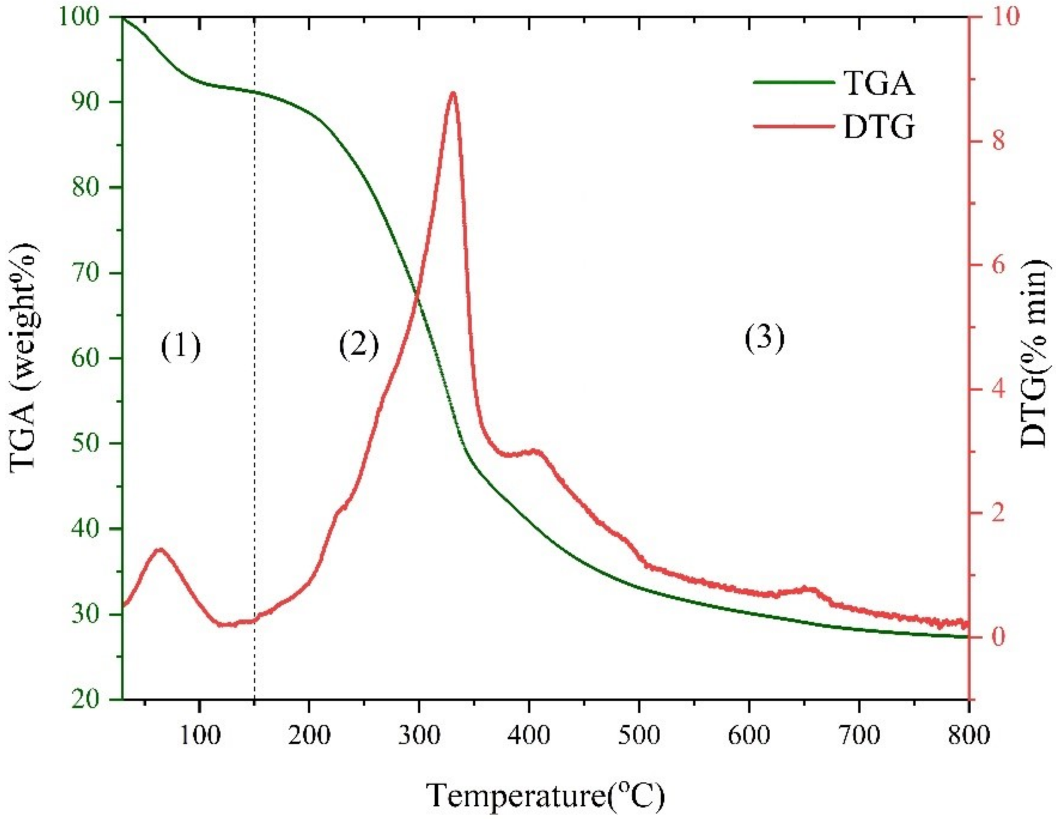

Fig. S8 Thermogravimetric and differential analysis of raw pine needles [1].

1.1.1. TGA and DTG

The TGA/DTG analysis examined PN's thermal degradation behavior, as shown in Figure S7. The thermal degradation of PN was divided into three different stages. The first stage speaks of the valorization of high volatiles and moisture, due to which the PN degradation rate is slow in this stage (up to ~150 ^{o}C). Stage second (160-450 ^{o}C) exhibits the highest rate of PN degradation, representing the conversion of holocellulose illustrated by the peak at 320 ^{o}C. At the same time, the valorization of lignin and char formation is associated with stage three (450-800 ^{o}C), denoted by the different number of peaks in the wide temperature range. However, these processes can overlap and can't be clearly distinguished [2]. Havilah et al.[3] reported the maximum devolatilization in the range 190 to 450 °C attributed to cellulose and hemicellulose, whereas the degradation of lignin corresponds to temperature 450 to 780 °C.

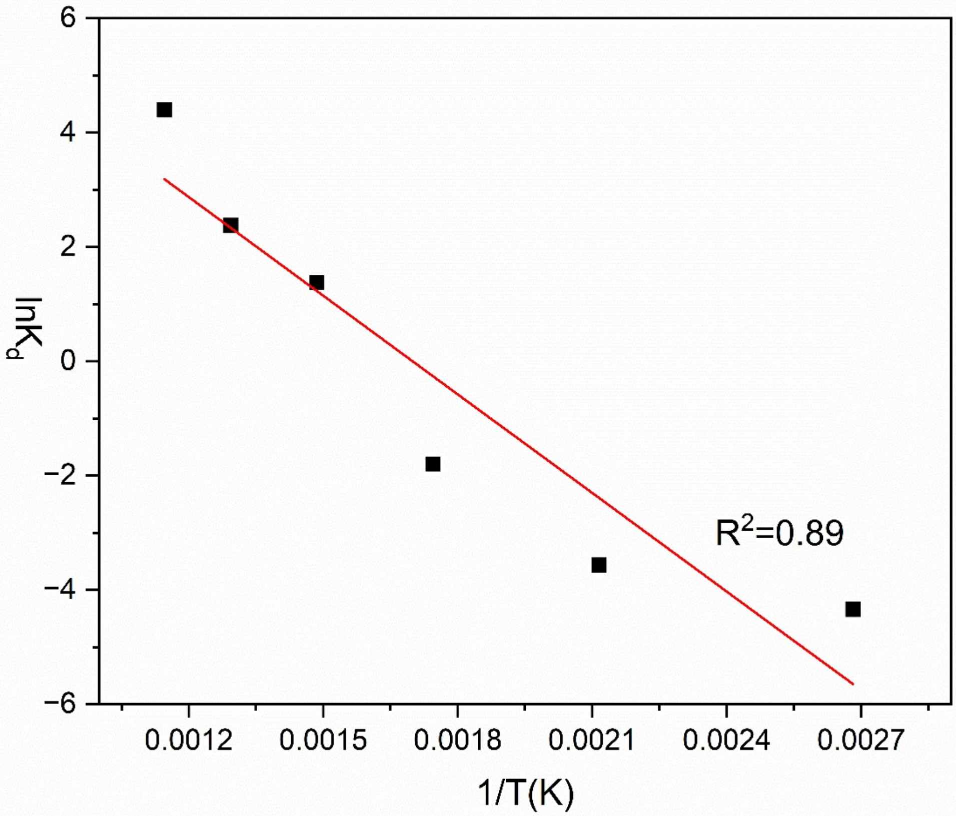

Fig .S9 Vont hoff model

Table S1. Initial characterization of real zinc electroplating wastewater (Zn-EPE) and simulated metal effluent.

Metal Effluent	**Metals**	**Concentration (ppm)**	**Conductivity (mS)**	**TDS (ppt)**	**pH**
	Zinc	765			
	Iron	23			
Zn-EPE	Copper	25	0.38	0.19	2.2
	Nickel	28			
	Chromium	506			
Zn-SME	Zinc	1758	3.6	1.8	4.2

Table S2. Specific surface area and total pore volume of carbon composite sample obtained at 0 min, 30 min and 60 min residence time.

Sample	**Surface area ($m^2.g^{-1}$)**	**Total pore volume ($cm^3.g^{-1}$)**
0 min	14.9	$5.5x10^{-2}$

30 min	122.2	$9.2x10^{-2}$
60 min	221.1	$1.36x10^{-1}$

Table.S3 Ultimate and proximate analysis of pine needles [1].

Proximate analysis			Ultimate analysis							
Volatile content (%)	Ash Content (%)	Fixed Carbon (%)	C (%)	H (%)	N (%)	S (%)	O^a (%)	O/C	H/C	N/C
73.5	2.1	24.4	47.8	6.8	0.9	--	42.4	0.7	1.7	0.02
Empirical Formula			$CH_{1.7}O_{0.7}N_{0.02}$							
HHV(MJ/Kg)			19.16							

(a) Oxygen (O)=100-(C+H+N+Ash) %

Ultimate and proximate analysis of feedstock

The quality and quantity of products generated via. thermochemical treatment of biomass depends on the elemental (C, H, and O) composition of biomass, along with the moisture, volatile, and ash content. Therefore, the ultimate and the proximate pine needles (PN) analysis was carried out as given in Table S3. The proximate analysis of PN illustrates that it contains high volatile content (~73.5 %) and low ash content (~2.1 %), ensuring the feasibility of using pine needles for thermal degradations. The higher quantity of ash content is not desired for thermochemical treatment as it leads to slag formation and fouling, leading to reduced process efficiency [4,5]. The ultimate analysis was performed to determine the elemental composition of pine needles. The percentage of carbon, oxygen, and hydrogen in pine needles is found to be 47.8 %, 42.4 %, and 6.8 %, respectively, as well as negligible amounts of nitrogen (~0.9 %) and zero sulfur. The lower percentage of nitrogen and sulfur in biomass illustrates that upon thermochemical conversion, negligible quantities of SO_x and NO_x were produced. Similarly, Mandal et al. [6] reported that pine needles contain 49.47% carbon, 34.12% oxygen, and 1.05% nitrogen, which are the typical value of biomass.

Table. S4 Thermodynamic parameters for adsorption of zinc metal in hydrothermal process

Temperature (K)	ΔG° ($kcal.mol^{-1}$)	ΔH° ($kcal.mol^{-1}$)	ΔS° ($kcal.mol^{-1}$)
373	13.46	47.81	0.08
473	14.00		
573	8.565		
673	-7.70		
773	-15.300		
873	-31.92		

References

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