Nutrient recovery from hydrothermal treatment of food waste

Andrés Sarrión*, Elena Diaz, Angeles de la Rubia, Angel F. Mohedano

Department of Chemical Engineering, Faculty of Science, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049, Madrid (Spain)

*andres.sarrion@uam.es

Abstract

Hydrothermal carbonization was evaluated as a food waste valorization strategy to obtain a solid fuel (hydrochar) and to recover nutrients (P, N and K). In the hydrothermal treatment, variables such as temperature (170 - 230 ºC), reaction time (5 - 60 min) and the addition of HCl to the reaction medium (0.1 - 0.5 M) were analyzed. Compared to the feedstock, the hydrochars showed an increase in fixed carbon (> 45 %), a decrease in volatile matter (< 65 %) and ash content (< 7 %), and high higher heating value (18.6 - 26.2 MJ/kg), which allows their direct application as solid fuel for industrial application, according to ISO 17225-8. The hydrochars obtained in the absence of HCl showed a high P and N content, around 75 and 40 % of the feedstock content. Acid mediated treatment with HCl allowed solubilizing most of the N and P in the process water (98 % P, as PO_4-P, 98 % K and almost the total N content, being 16 % NH_4-N and the rest organic N), operating at 170 °C for 60 min and incorporating 0.5 M HCl.

Keywords: Biomass valorization, hydrochar, hydrothermal carbonization, nutrient recovery, food waste, solid biofuel.

1. Introduction

Currently, one of the most worrying social problems focuses on the inadequate management of waste generation, which causes several negative impacts on the environment such as soil and water pollution, excessive depletion of natural resources, degradation of ecosystems and a progressive worsening of the health [1]. In 2019, more than 2,000 million tonnes of municipal solid waste (MSW) were generated worldwide and it is estimated to increase up to 70 % by 2050, with 44 % corresponding to the organic fraction of municipal waste (OFMW), mainly composed by food waste [2]. This high increase is attributed to rapid population growth, high urban overcrowding or an inefficient production system that shortens the lifetime of the materials [3]. The current European legislation in terms of biowaste management establishes some actions to minimize their impact on environment through a circular economic policy based on the reduction of the carbon footprint of waste through useful knowledge of eco-friendly management [4].

Food waste consist mainly of organic compounds and mineral salts [5], including a significant concentration in essential nutrients (mainly phosphorus, nitrogen and potassium), whose scarcity in natural sources makes it necessary to find new ways of recovery [6]. These nutrients are the main components of any fertilizer for agricultural application [7], crucial to attend the needs of the huge population growth in the coming years (up to 9,700 million people in 2050) [8]. Furthermore, the opportunity to recover nutrients from food waste is coupled with the achievement of the current European Directive 2018/851, focused on recovering more than 50 % of biowaste-based materials through recycling by 2025 and managing them through a non-conventional alternative to landfilling.

In addition to biological processes (mainly composting and anaerobic digestion), thermochemical conversion represent a feasible route for handling food waste. In this framework, hydrothermal carbonization (HTC) emerges as a technology that allows the recovery of nutrients from biowaste with a high degree of moisture together with a subsequent energy valorization of the feedstock. HTC is an exothermic thermochemical process in which the wet feedstock is treated at 170-250 ºC and with low residence times (5-240 min) under self-generated pressure. Though hydrolysis, condensation, aromatization, dehydration and decarboxylation reactions, a carbon-rich solid product, known as hydrochar (HC), with fuel properties similar to those of lignite, a process water (PW) containing inorganic salts and organic compounds, and a gaseous stream consisting mainly of CO_2 are obtained [9]. Due to the physical and energetic properties of hydrochar, its main potential applications include its use as solid fuel [10,11], catalyst support [3,12], activated carbon precursor [13,14], soil amendment [15], energy storage in batteries, fuel cells or supercapacitors [16,17], as well as being used directly as an alternative nutrient source [18].

Table 1 provides information on nutrient recovery from biomass waste. The simplest strategy is based on direct acid washing of biomass [19,20]. Some authors have examined the possibility of HTC-mediated nutrient recovery from biomass as a strategy to promote nutrient leaching to the PW [21,22] or their concentration in HC [18,23]. Acid-mediated HTC as an option to facilitate the release of N and P from biomass has been scarcely studied despite interesting results obtained by Dai et al. [24], Ekpo et al. [25] and Qaramaleki et al. [26]. In this sense, the aim of this work is to study the fate of nutrients (N, P and K), in the HC and PW obtained in the HTC of food waste at various temperatures (170-230 ºC), residence times (5-60 min), including the possibility of adding HCl (0.1-0.5 M) during carbonization process.

2. Materials and methods

2.1. Food waste

Food waste was collected from a local management plant operating in a food distribution platform (Madrid, Spain). The raw food waste was grinded and stored in 1.5 kg portions at -20 ºC to facilitate its preservation. In each experiment, moisture of defrosted portions of food waste was measured (91 - 93 wt. %). **Table 2** shows the main characteristics of the feedstock.

2.2. Hydrothermal carbonization experiments

Hydrothermal experiments were carried out in an electrically heated ZipperClave stirred pressure vessel (4 L). In each run, the reactor was loaded with 1.5 kg of defrosted feedstock. The operating temperature (170-230 ºC) was reached by heating the reactor at a rate of 3 ºC min^{-1} and holding the selected temperature for 1 h. The effect of temperature and HCl addition (0.1-0.5 M) was studied using response surface methodology based on a fractional factorial design with a duplicate central point. Using Minitab 19 software, 3 acid-free experiments and 6 acid-mediated experiments (4 factorial points and 2 replicates of the central point) were generated. Each experiment was performed by duplicated.

Samples of process water (40 mL) were withdrawn from the reactor at 5, 15, 30 and 60 min using a sample collection system. The reaction was stopped after 60 min by cooling with an internal heat exchanger using tap water. The slurry (HC and PW) was then separated by filtration using 250 μm membrane vacuum filters. HC was obtained by oven drying the solid fraction overnight at 105 ºC with subsequent grounding and sieving to a particle size between 100 and 200 μm. The PW was filtrated through 0.45 μm Scharlab glass filters and stored at 4 ºC. The mass yield of HC (Y_{HC}) was defined as the weight ratio of recovered HC (W_{HC}) to food waste feedstock (W_{FW}) on a dry basis (**equation 1**).

$$Y_{HC}\ (\%) = (W_{HC}/W_{FW}) \cdot 100 \qquad (1)$$

The yield of PW (Y_{PW}) was calculated as the ratio of the volume of PW recovered (V_{PW}) to the liquid volume of the raw food waste (V_{FW}) (**equation 2)**.

$$Y_{PW}\ (\%) = (V_{PW}/V_{FW}) \cdot 100 \qquad (2)$$

2.3. Phosphorus, nitrogen and potassium leaching from the hydrochar

A sample of HC (10 g) from acid-free HTC (170-230 ºC) was treated with 100 mL of 0.5 M HCl using an orbital shaker for 2 h for the extraction of P, N and K. The resulting leachate and washed HC were separated by vacuum filtration for further analysis.

2.4. Analytical methods

The elemental composition (C, H, N and S) of the PW, leachate and HC samples (including washed HC) was determined on a CHNS analyzer (LECO CHNS-932). Oxygen content was calculated by difference. Proximate analysis was performed according to ASTM methods D3173-11, D3174-11, and D3175-11, to determine moisture, ash, volatile matter (VM) and fixed carbon (FC) content (by difference). The HHV of dried solid samples was determined using **equation 3**, a correlation for calculating HHV from elemental composition (in percentage) according to Channiwala and Parikh [27].

$$HHV\ (MJ/kg) = 0.349\ C + 1.178\ H + 0.100\ S - 0.103\ O - 0.015\ N\ - 0.021\ Ash \qquad (3)$$

The concentration of other mineral elements was quantified by inductively coupled optical emission spectroscopy (ICP-OES) on a ThermoFisher Scientific IRIS INTREPID II XDL instrument. A known volume of liquid sample was digested with 10 mL of concentrated H_2SO_4 in the presence of a copper-based catalyst to determine the ammonium (NH_4-N) and organic nitrogen (Org-N) content (which is converted to ammonium) by the Kjeldahl method. The digested samples were mixed with NaOH (6 N, PanReac) to convert ammonium to ammonia and then distilled into 50 mL H_3BO_3 solution, which was titrated with H_2SO_4 (0.02 N, PanReac) to measure the total Kjeldahl nitrogen (TKN). To determine the NH_4^+-N content, aliquots of PW samples were used directly in the distillation step without prior digestion. Subsequently, titration was carried out as the determination of TKN. Nitrite (NO_2^-) and nitrate (NO_3^-) were quantified on a Dionex ICS-900 ion chromatograph with chemical suppression and fitted with a Dionex IonPac AS22 4 × 250 mm column, using a 1 mL min^{-1} mobile phase 1.4/4.5 mM of $NaHCO_3$ and Na_2CO_3, respectively. Ortho-PO_4^{3-} in the PW and leachates was analysed photometrically with a Hach Lange LCK350 cuvette test. On the other hand, the Standards Measurements and Testing (SMT) protocol [28] was applied in washed HC to analyze its residual P speciation. Total P was extracted by mixing 0.2 g of HC (previously calcinated for 3 h at 450 ºC) with 20 mL of HCl 3.5 M under continuous stirring for 16 h at room temperature. Ortho-PO_4^{3-} was extracted by mixing 0.2 g of HC with 20 mL of 1 M HCl under continuous stirring for 16 h at 25 ºC.

3. Results and discussion

3.1. Characterization of raw food waste and resulting hydrochar

Table 2 shows the proximate and final analysis of the feedstock and HC resulting from the HTC after 60 min. The crude food waste contains 7.2 wt.% solid content, low fixed carbon (FC) content due to the high amount of volatile matter (VM) derived from the high content of organic compounds in the feedstock [29]. HHV was in the range of biomass fuels (15-20 MJ/kg) due to its low carbonaceous composition and high oxygen content [30].

With regard to hydrochars, the HC yield showed a remarkable decrease with increasing carbonization temperature, especially in the presence of HCl and temperatures above 170 °C (Table 2), which promote degradation reactions and solubilization of organic matter to the PW [23,31]. The FC of HC increased with carbonization temperature, as a consequence of the volatilization of oxygen-containing functional groups, which may allow for a more constant and stable flame during combustion and a higher fuel firing temperature [32]. The ash content in HC obtained in the absence of acid increased with increasing temperature, because the inorganic compounds present in the feedstock remain in the solid phase after heat treatment. In HCl-mediated HTC, the HC have lower ash content as they solubilize in the process water, improving the suitability of the acid-washed coal for use as clean fuel.

The elemental composition of the HC shows an increase in carbon content and a decrease in oxygen content with carbonization temperature and acid concentration used. The hydrogen content was not affected by temperature or acid addition, so the O/C and H/C atomic ratios decreased, indicating an increase in the degree of carbonization of the HC, due to dehydration, carboxylation and condensation reactions [13]. The sulphur content remained below 0.3 wt. % in all cases. The HHV of HC was similar to that of lignite [33]. Thus, the HHV of HC from acid-free HTC gradually increased with temperature to values 25 % higher than that of the feedstock. In acid-mediated carbonization, a significant increase in HHV was observed, reaching a value of 26.2 MJ/kg using a temperature of 230 °C and 0.5 M HCl, related to the low yield at HC (27.2 wt. %). The HHV values were comparable to those obtained from other food waste [34] or different bio-waste such as pig manure [25], sewage sludge [35] and pruning waste [11]. The fixed C content of HC obtained with HCl addition, and the reduced values in N, S, and ash content allow meeting the current parameters of energy recovery from biomass, according to ISO 17225-8, as a promising alternative biofuel.

3.2. Nutrient recovery from hydrochar

The HC obtained by plain HTC were washed with HCl to extract P and N. Fig. 1 shows the distribution of total P (as PO_4^{3-}), N and K extracted in the leachate, as well as the content of these nutrients retained in the washed HC, and the corresponding recovery of P, N and K in the leachate with respect to the raw feedstock. The resulting HC retained 64.2, 93.8 and 99.8 % of the P initially present in the food waste at 170, 200 and 230 °C, respectively. The increase in P concentration with carbonization temperature could be related to the precipitation in the HC of insoluble PO_4^{3-} salts formed by cations present in the PW such as Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+} (see Fig. 3). HCl washing of these HC resulted in the release of 66 - 74 % of P from the HC. This contribution together with the existing P in the PW accounts for a recovery of 80 % of the initial P in the food waste working at 170 °C. Similar recovery was achieved by direct acid washing of fresh sewage sludge with 1 M H_2SO_4 for 2 h (65 % P recovery) [20], or from dried pig manure with 0.04 M HCl for 1 h (88 % P recovery) [19].

Nitrogen and potassium, however, were mainly concentrated in PW, with only 32.7, 38.9 and 40.6 wt. %, and 14.1, 22.8 and 24.6 wt. %, being retained in HC at 170, 200 and 230 °C, respectively. In contrast to P, acid washing of HC did not favour the release of N by acid extraction, with a small contribution in the range 8.7 - 16 %, compared to the N content of food waste. This behaviour could be related to the initial speciation of N in the raw feedstock, where proteins are hydrolyzed to amino acids under HTC conditions, to be released to the PW. In addition, a higher nitrate content than ammonium causes strong N bonds with solved compounds promoting salt precipitation in HC [36–38]. Therefore, a N and K recovery around 77 and 93 %, respectively, present in the raw food waste was concentrated in the aqueous phase, irrespective of the carbonization temperature.

3.3. Nutrient recovery from process water

3.3.1. Fate of phosphorus

Fig. 2a shows the evolution of the P concentration in the PW, which is in all cases in the form of PO_4^{3-}, throughout the HTC process. In the absence of acid, the P concentration reached its maximum at 5 min of reaction, reaching a significantly higher value in the carbonization carried out at 170 °C (0.2 g P/L), equivalent to 2.3 g P/kg food waste. From that time onwards, the P concentration decreased progressively at the tested temperatures, which is attributed to the integration of P in the HC by precipitation of PO_4^{3-} with dissolved metallic elements along the reaction [39]. Fig. 3a,b shows the time evolution of the main dissolved cations, Ca^{2+}, Fe^{2+}, Mg^{2+} and Al^{3+}, in the reaction medium for the HTC reactions performed at 170 and 230 ºC, respectively. At the lowest temperature (170 ºC), mainly the decrease of Ca^{2+} and P concentration was observed, indicating the formation of calcium phosphate salts, which precipitates in the HC. At 230 °C, the decrease in Ca^{2+} concentration is much smaller, as is the concentration of PO_4^{3-} in the PW.

In HCl-mediated HTC (Fig. 2b), P concentration in the PW decreases with increasing temperature and, for the same temperature, increases with increasing HCl concentration. The addition of mineral acids in the HTC process has been beneficial for P extraction to PW in the hydrothermal treatment of pig manure [25] and cow manure [26]. The positive effect of HCl addition on P extraction decreases significantly with increasing temperature from 170 to 200 °C and above. In the 170 °C test with 0.5 M HCl, a P concentration of 0.44 g/L (equivalent to 4.9 g P/kg food waste) was observed in the PW, a value three times higher than that obtained in the experiments without acid addition at the same temperature. In the 0.5 M HCl mediated carbonization at 170 ºC (Fig. 3c), the concentration of Ca^{2+} and Fe^{2+} increases throughout the reaction favouring the presence of P in the PW. At 230 ºC (Fig. 3d) this trend is not observed, maintaining these cations at a almost constant concentration.

Fig. 4a shows the response surface of total TP recovery (as PO_4-P) versus temperature and acid concentration at 60 min, the time at which the highest P concentration is reached in the PW. The evolution of the P recovery was fitted to **equation 4**:

$$TP = 2.8283 - 0.01239 \cdot T - 0.708 \cdot C + 0.00725 \cdot T \cdot C \qquad (4)$$

where T is the HTC temperature (ºC), C is the HCl concentration (M) and TP is the fraction of P recovered in the PW. A diagnostic analysis (R^2 (99.93 %) and p-value (< 0.05)) validated the model and showed that the correlation was well fitted and adequate to predict an evolution of P recovery, close to that obtained with the experimental results. P recovery increased with decreasing temperature and increasing HCl addition, reaching a 98 % recovery of P from food waste at 60 min for 0.5 M HCl-mediated HTC at 170 ºC. In the non-acid experiments, P recovery significantly decreased (32.9 % P recovery in PW at 170 °C). The P recovery obtained using 0.5 M HCl is significantly higher than that obtained with food waste (70 % P recovery at 225 °C) [21], and even higher than those obtained for other P-rich biowaste such as sewage sludge (82 % P recovery after HTC at 230 °C) [40] or manure (92 % P recovery after HTC mediated by 0.1 M H_2SO_4 at 170 °C) [25].

3.3.2. Fate of nitrogen

A complementary analysis on N recovery in the PW was performed. Fig. 2c,d shows the evolution of the N concentration in the PW resulting from acid-free and HCl-mediated HTC, respectively. In the acid-free experiments (Fig. 2c), the N concentration in the PW was similar after 5 min of reaction at the three temperatures studied (1.8 g N/L), with a slight decrease of this concentration over the reaction time in the PW obtained at 200 and 230 °C. This fact could be attributed to the related effective adsorption properties of HC, causing the sorption of nitrogen-containing substances at higher temperature and reaction time [41,42].

In the case of HCl-mediated HTC (Fig. 5b), a noticeable effect of acid on the increase of N concentration in the PW was observed because of the hydrolysis of nitrogen-bearing organic compounds [25, 29]. With the lowest HCl addition (0.1 M), the maximum N concentration in the PW occurs at 170 °C, highlighting that an increase in HTC temperature is not associated with an increase in N leaching, while practically the same results, in terms of N concentration in the aqueous phase, were obtained along HTC at 170 and 230 °C with 0.5 M HCl. In these latter conditions, N concentration in the PW reaches 2.8 g/L (corresponding to 30.4 g N/kg food waste), showing no significant differences along time. The positive effect of acid addition during HTC was previously observed by Dai et al. [24], who studied HCl-mediated manure HTC, achieving 64 % initial N concentration in the PW at the optimal operating conditions (190 °C and 0.6 M HCl) versus 39 % initial N recovery at 190 °C in the absence of acid.

The analysis of the N compounds present in the PW (Fig. 5) showed that the majority nitrogen species, in the reaction carried out in the absence of acid, were nitrate (74-78 %) and ammonium (21-23 %), regardless of temperature employed. In the acid-mediated reactions, the N concentration in form of nitrogen-bearing organic compounds increased up to 55 % at 170 ºC and 0.5 M HCl, which could mainly be amino acids from hydrolysis of proteins, and their subsequent decomposition to NH_4-N under hydrothermal conditions [24,36,43]. In the reactions with the highest HCl concentration (0.5 M), the presence of nitrate decreases significantly (24-27 %) and practically no nitrite is observed (< 0.1 %), so they have not been considered in the following analysis.

Again, Fig. 4b,c shows the response surface of N recovery in process water (as total nitrogen and as ammonia nitrogen) at 60 min of reaction. Equations (5) and (6) describe the evolution of total N and, also, NH_4-N recovery in PW as a function of temperature and HCl concentration. The statistical parameters obtained ($p < 0.05$ and $R^2 > 99.7$ %) validate the response surfaces shown.

$$TN = 1{,}26 - 0{,}0026 \cdot T - 0{,}46 \cdot C + 0{,}005 \cdot T \cdot C \tag{5}$$

$$TNH_4 - N = 0{,}18 - 0{,}00015 \cdot T - 0{,}23 \cdot C + 0{,}0015 \cdot T \cdot C \tag{6}$$

where, TN_L and TNH_4-N the fraction of total N and NH_4, as N concentration, recovered in the PW, respectively.

As can be seen, the HCl concentration is crucial in the release of N to the PW. The maximum N recovery in the PW is achieved with 0.5 M HCl-mediated HTC at 170 °C, being slightly higher than that obtained with 0.5 M HCl at 230 °C. However, only 16 % of the TN was recovered as NH_4-N, because the corresponding transformation of the released organic N to NH_4 is favoured with reaction time and HTC temperature. In this sense, at 230 °C and 0.5 M HCl the amount of NH_4-N in the PW increased by about 7 % over the reaction time, being 22 % higher than that obtained when the temperature was 170 °C. Then, HCl-mediated HTC of food waste seems to be a promising process allowing improved N recovery compared to other biomasses such as manure, treated by Szögi et al. [19] with direct acid washing with HCl at ambient conditions (47 % N recovery) or, more recently, by Dai et al. [24] in HCl-mediated HTC of cow manure at 190 °C for 12 h (recovered 63 and 45 % of total N and NH_4-N, respectively).

3.3.3. Fate of potassium

The highest K extraction in PW was observed at the lowest temperature (170 °C), and its concentration increased with reaction time in all cases. These results were expected due to the high solubility of K in water. Acid-mediated HTC enhanced the solubility of K in PW, with the highest K concentration being obtained at 170 °C using 0.5 M HCl (37.5 g K/kg food waste). The response surface study for K recovery (Fig. 4d) yielded equation 7 ($p < 0.05$ and $R^2 > 99.7$ %).

$$TK = 1{,}11 - 0{,}00093 \cdot T - 0{,}26 \cdot C + 0{,}0019 \cdot T \cdot C \tag{7}$$

where TK is the fraction of total K recovered in the PW. As can be seen, K was almost completely extracted (more than 90 % of the initial K) for any of the temperatures and acid concentration used, the latter being the most relevant variable. The highest K recovery in the PW (98 % of the K in the feedstock) was achieved with 0.5 M HCl-mediated HTC, irrespective of the temperature used.

4. Conclusions

Hydrothermal carbonization emerges as an interesting way to valorize food waste into solid biofuels, also allowing nutrient (N, P and K) recovery. Solubilization of nutrients by plain HTC was temperature dependent. In general, a soft temperature (170 ºC) is recommended to improve the nutrient recovery in aqueous phase after optimal reaction time of 60 min. However, the addition of HCl during hydrothermal carbonization was crucial to maximize the recovery of N (mostly formed by organic-N and NH_4), P (in form of PO_4^{3-}) and K directly in the process water.

Additionally, HTC technology allows to obtain hydrochar with attractive characteristics to be used in industry as solid biofuel. Thus, these results suggested that HTC mediated by HCl simultaneously facilitate nutrient recovery from food waste and upgrade the resulting hydrochar.

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.

CRediT authorship contribution statement

Andrés Sarrión: Investigation, Formal analysis, Writing – original draft. **Elena Díaz**: Conceptualization, Formal analysis, Funding acquisition, Methodology, Resources, Writing - review & editing, Supervision. **M. Angeles de la Rubia:** Funding acquisition, Writing - review & editing, Supervision. **Angel F. Mohedano:** Conceptualization, Funding acquisition, Methodology, Resources, Writing - review & editing, Supervision, Project administration.

Acknowledgements

Authors greatly appreciate funding from Spanish MICINN (Project PID2019-108445RB-I00) and Madrid Regional Government (Project S2018/EMT-4344). A. Sarrión wishes to thank the Spanish MICINN and the ESF for a research grant (BES-2017-081515). Authors thank Silvia Rodríguez for her valuable help.

References

[1] Vallero D.A.: Effect of waste on ecosystems. 2nd ed. Elsevier Inc., Durham, NC (2019).

[2] World bank: What a Waste: an updated look into the future of solid waste management. https://www.worldbank.org/en/news/immersive-story/2018/09/20/what-a-waste-an-updated-look-into-the-future-of-solid-waste-management (2018) Accessed 20 March 2021.

[3] Tang Z., Li W., Tam V.W.Y., Xue C.: Advanced progress in recycling municipal and construction solid wastes for manufacturing sustainable construction materials. Resour. Conserv. Recycl. X 6, 100036 (2020).

[4] European Commission: A new circular economy action plan for a cleaner and more competitive Europe. Brussels https://doi.org/https://www.un.org/sustainabledevelopment/sustainable-consumption-production/ (2020) Accesed 26 March 2021.

[5] Panigrahi S., Dubey B.K.: A critical review on operating parameters and strategies to improve the biogas yield from anaerobic digestion of organic fraction of municipal solid waste. Renew. Energy 143, 779–97 (2019).

[6] Zhao X., Becker G.C., Faweya N., Rodriguez Correa C., Yang S., Xie X.: Fertilizer and activated carbon production by hydrothermal carbonization of digestate. Biomass Convers. Biorefinery 8, 423-436 (2018).

[7] Ostadi A., Javanmard A., Amani Machiani M., Morshedloo M.R., Nouraein M., Rasouli F.: Effect of different fertilizer sources and harvesting time on the growth characteristics, nutrient uptakes, essential oil productivity and composition of Mentha x piperita L. Ind. Crops Prod. 148, 112290 (2020).

[8] Kjerstadius H., Haghighatafshar S., Davidsson A.: Potential for nutrient recovery and biogas production from blackwater, food waste and greywater in urban source control systems. Environ. Technol. 36, 1707–20 (2015).

[9] Kumar M., Olajire Oyedun A., Kumar A.: A review on the current status of various

hydrothermal technologies on biomass feedstock. Renew. Sustain. Energy Rev. 81, 1742–70 (2018).

[10] He C., Giannis A., Wang J.Y.: Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. Appl. Energy 111, 257–66 (2013).

[11] Sharma H.B., Panigrahi S., Dubey B.K.: Hydrothermal carbonization of yard waste for solid bio-fuel production: Study on combustion kinetic, energy properties, grindability and flowability of hydrochar. Waste Manag. 91, 108–19 (2019).

[12] Ge X., Ge M., Chen X., Qian C., Liu X., Zhou S.: Facile synthesis of hydrochar supported copper nanocatalyst for Ullmann CN coupling reaction in water. Mol. Catal. 484, 110726 (2019).

[13] Diaz E., Manzano F.J., Villamil J., Rodriguez J.J., Mohedano A.F.: Low-Cost Activated Grape Seed-Derived Hydrochar through Hydrothermal Carbonization and Chemical Activation for Sulfamethoxazole Adsorption. Appl. Sci. 9, 5127 (2019).

[14] Fernandez M.E., Ledesma B., Román S., Bonelli P.R., Cukierman A.L.: Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants. Bioresour. Technol. 183, 221–8 (2015).

[15] Xia Y., Luo H., Li D., Chen Z., Yang S., Liu Z.: Efficient immobilization of toxic heavy metals in multi-contaminated agricultural soils by amino-functionalized hydrochar: Performance, plant responses and immobilization mechanisms. Environ. Pollut. 261, 114217 (2020).

[16] Wilk M., Magdziarz A., Jayaraman K., Szymańska-Chargot M., Gökalp I.: Hydrothermal carbonization characteristics of sewage sludge and lignocellulosic biomass. A comparative study. Biomass and Bioenergy 120, 166–75 (2019).

[17] Niu Z., Feng W., Huang H., Wang B., Chen L., Miao Y.: Green synthesis of a novel

Mn–Zn ferrite/biochar composite from waste batteries and pine sawdust for Pb2+ removal. Chemosphere 252, 126529 (2020).

[18] Becker G.C., Wüst D., Köhler H., Lautenbach A., Kruse A.: Novel approach of phosphate-reclamation as struvite from sewage sludge by utilising hydrothermal carbonization. J. Environ. Manage. 238, 119–25 (2019).

[19] Szögi A.A., Vanotti M.B., Hunt P.G.: Phosphorus recovery from pig manure solids prior to land application. J. Environ. Manage. 157, 1–7 (2015).

[20] Shiba N.C., Ntuli F.: Extraction and precipitation of phosphorus from sewage sludge. Waste Manag. 60, 191–200 (2017).

[21] Idowu I., Li L., Flora J.R.V., Pellechia P.J., Darko S.A., Ro K.S.: Hydrothermal carbonization of food waste for nutrient recovery and reuse. Waste Manag. 105, 566–74 (2017).

[22] Ekpo U., Ross A.B., Camargo-Valero M.A., Williams P.T.: A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioresour. Technol. 200, 951–60 (2015).

[23] Heilmann S.M., Molde J.S., Timler J.G., Wood B.M., Mikula A.L., Vozhdayev G. V.: Phosphorus reclamation through hydrothermal carbonization of animal manures. Environ. Sci. Technol. 48, 10323–9 (2014).

[24] Dai L., Yang B., Li H., Tan F., Zhu N., Zhu Q.: A synergistic combination of nutrient reclamation from manure and resultant hydrochar upgradation by acid-supported hydrothermal carbonization. Bioresour. Technol. 243, 860–6 (2017).

[25] Ekpo U., Ross A.B., Camargo-Valero M.A., Fletcher L.A.: Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus in process water. Bioresour. Technol. 214, 637–44 (2016).

[26] Qaramaleki S. V., Villamil J.A., Mohedano A.F., Coronella C.J.: Factors affecting solubilization of phosphorus and nitrogen through hydrothermal carbonization of animal manure. ACS Sustain. Chem. Eng. 8, 12462–70 (2020).

[27] Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81, 1051–63 (2002).

[28] Pardo P., Rauret G., López-Sánchez J.F.: Shortened screening method for phosphorus fractionation in sediments: A complementary approach to the standards, measurements and testing harmonised protocol. Anal. Chim. Acta 508, 201–6 (2004).

[29] Liu Z., Zhang Y., Liu Z.: Comparative production of biochars from corn stalk and cow manure. Bioresour. Technol. 291, 121855 (2019).

[30] Pradhan P., Mahajani S.M., Arora A.: Production and utilization of fuel pellets from biomass: A review. Fuel Process. Technol. 181, 215–32 (2018).

[31] Jiang Z., Meng D., Mu H., Yoshikawa K.: Study on the hydrothermal drying technology of sewage sludge. Sci. China Technol. Sci. 53, 160-163 (2010).

[32] He C., Giannis A., Wang J.Y.: Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. Appl. Energy 111, 257–66 (2013)

[33] Engin B., Atakül H., Ünlü A., Olgun Z.: CFB combustion of low-grade lignites: Operating stability and emissions. J. Energy Inst. 92, 542–53 (2019).

[34] Saqib N.U., Sharma H.B., Baroutian S., Dubey B., Sarmah A.K.: Valorisation of food waste via hydrothermal carbonisation and techno-economic feasibility assessment. Sci. Total Environ. 690, 261–76 (2019).

[35] Zheng C., Ma X., Yao Z., Chen X.: The properties and combustion behaviors of hydrochars derived from co-hydrothermal carbonization of sewage sludge and food waste. Bioresour. Technol. 285, 121347 (2019).

[36] Kruse A., Koch F., Stelzl K., Wüst D., Zeller M.: Fate of nitrogen during hydrothermal carbonization. Energy Fuels 30, 8037–42 (2016).

[37] Peterson A.A., Lachance R.P., Tester J.W.: Kinetic evidence of the maillard reaction in hydrothermal biomass processing: Glucose-glycine interactions in high-temperature, high-pressure water. Ind. Eng. Chem. Res. 49, 2107–17 (2010).

[38] Zhang Y., Jiang Q., Xie W., Wang Y., Kang J.: Effects of temperature, time and acidity of hydrothermal carbonization on the hydrochar properties and nitrogen recovery from corn stover. Biomass and Bioenergy 122, 175–82 (2019).

[39] Chen B., Chen Z., Lv S.: A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresour. Technol. 102, 716–23 (2011).

[40] Munir M.T., Li B., Mardon I., Young B.R., Baroutian S.: Integrating wet oxidation and struvite precipitation for sewage sludge treatment and phosphorus recovery. J. Clean. Prod. 232, 1043–52 (2019).

[41] Regmi P., Garcia Moscoso J.L., Kumar S., Cao X., Mao J., Schafran G.: Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. J. Environ. Manage. 109, 61–9 (2012).

[42] Reza M.T., Freitas A., Yang X., Hiibel S., Lin H., Coronella C.J.: Hydrothermal Carbonization (HTC) of cow manure : carbon and nitrogen distributions in HTC products. Environ. Prog. Sustainable Energy 35, 1002–1011 (2016).

[43] Sato N., Quitain A.T., Kang K., Daimon H., Fujie K.: Reaction kinetics of amino acid decomposition in high-temperature and high-pressure water. Ind. Eng. Chem. Res. 43, 3217–22 (2004).

Highlights

- Promoting the nutrient recovery from food waste through hydrothermal carbonization (HTC).
- Acid-mediated HTC improved hydrochar properties as a solid fuel.
- Low HTC temperature (170 ºC) and acid-mediated (0.5 M HCl) HTC favoured nutrient extraction to process water.
- Acid-mediated HTC increased the extraction of N and P as NH_4-N and PO_4-P.

Graphical abstract

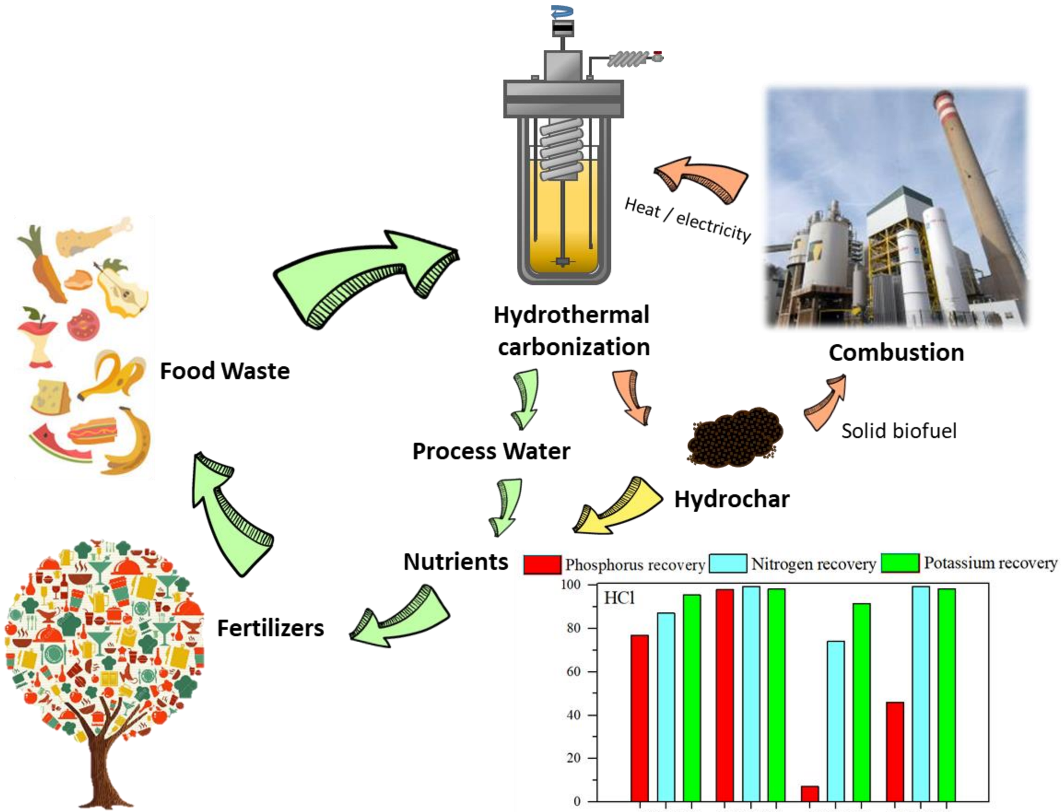

Table 1. Summary of optimal operating conditions and recovery percentage (in dry basis) of nutrients from biomass waste.

Treatment	Waste biomass	Nutrients in feedstock (%)			Operating conditions	Nutrient recovery (%)			Reference
		N	**P**	**K**	**Time (min) / T (ºC) / Acid reagent**	**N**	**P**	**K**	**-**
Acid wash	Pig manure	0.8	0.4	-	1 / 25 / HCl 0.04 M	47	88	-	Szögi et al., 2015
	Sewage sludge	-	1.5	-	2 / 100 / H_2SO_4 1 M	-	65	-	Shiba et al., 2017
HTC	Food waste	3.2	0.4	0.5	24 / 225 / -	50	70	96	Idowu et al., 2017
	Microalgae	9.7	2.2	0.5	1 / 250 / -	63	39	100	Ekpo et al., 2015
HTC + Acid wash	Pig manure	4.9	1.7	-	2 / 250 / HCl 0.4 M	-	89	-	Heilmann et al., 2014
	Sewage sludge	3.7	3.1	-	2 / 190 / Citric acid 2 M	-	95	-	Becker et al., 2019
Acid-mediated HTC	Cow manure	1.7	1.3	0.4	12 / 190 / HCl 0.6 M	64	96	90	Dai et al., 2017
	Pig manure	3.0	1.6	1.2	1 / 220- 250 / H_2SO_4 0.1 M	75	77	100	Ekpo et al., 2016
	Animal manure	1.8	0.4	0.4	0.1 / 170 / Citric acid 0.3 M	60	98	-	Qaramaleki et al. 2020

Table 2. Main characteristics of feedstock and hydrochar from HTC (dry basis)

Sample	T – HCl	Proximate analysis (wt. %)				Ultimate analysis (wt. %)					HHV (MJ/kg)
		Yield	FC	VM	Ash	C	N	S	H	O[a]	
Food waste		-	13.3±0.2	67.6±0.1	11.8±0.1	44.5±0.3	3.1±0.2	0.2±0.0	6.1±0.8	34.3±0.2	18.9±0.1
HC HTC	170 ºC	80.4±0.5	16.2±0.3	60.1±0.2	12.6±0.2	46.2±0.3	1.7±0.1	0.2±0.0	5.9±0.2	33.4±0.2	19.4±0.2
	200 ºC	67.7±2.2	19.0±0.4	57.8±1.6	13.6±0.3	48.6±0.1	2.0±0.2	0.2±0.0	5.7±0.2	29.4±0.2	20.3±0.2
	230 ºC	61.2±1.6	21.0±0.9	56.2±0.2	14.3±0.2	54.8±0.9	2.3±0.3	0.2±0.0	6.1±0.1	23.2±0.1	23.7±0.1
HC HTC-HCl	170 ºC - 0.1 M	55.5±1.2	21.0±0.5	62.7±0.2	7.8±0.2	45.8±0.1	1.2±0.0	0.2±0.0	5.7±0.2	39.3±0.2	18.6±0.2
	170 ºC - 0.5 M	28.0±0.6	28.2±0.2	53.4±0.9	6.4±0.1	56.1±0.2	0.3±0.0	0.3±0.0	6.0±0.2	30.9±0.2	23.3±0.2
	200 ºC - 0.3 M	39.2±0.8	39.5±2.3	41.7±1.1	7.5±0.4	54.0±0.1	1.2±0.0	0.3±0.0	6.0±0.1	31.0±0.1	22.6±0.1
	230 ºC - 0.1 M	48.2±1.8	44.9±0.1	41.5±0.2	6.8±0.3	56.1±0.1	2.2±0.1	0.3±0.0	5.9±0.2	25.8±0.2	23.7±0.2
	230 ºC - 0.5 M	27.2±2.3	48.9±0.3	35.5±0.2	4.7±0.4	62.1±0.2	0.5±0.0	0.3±0.0	6.2±0.2	26.2±0.1	26.2±0.1

[a] by difference

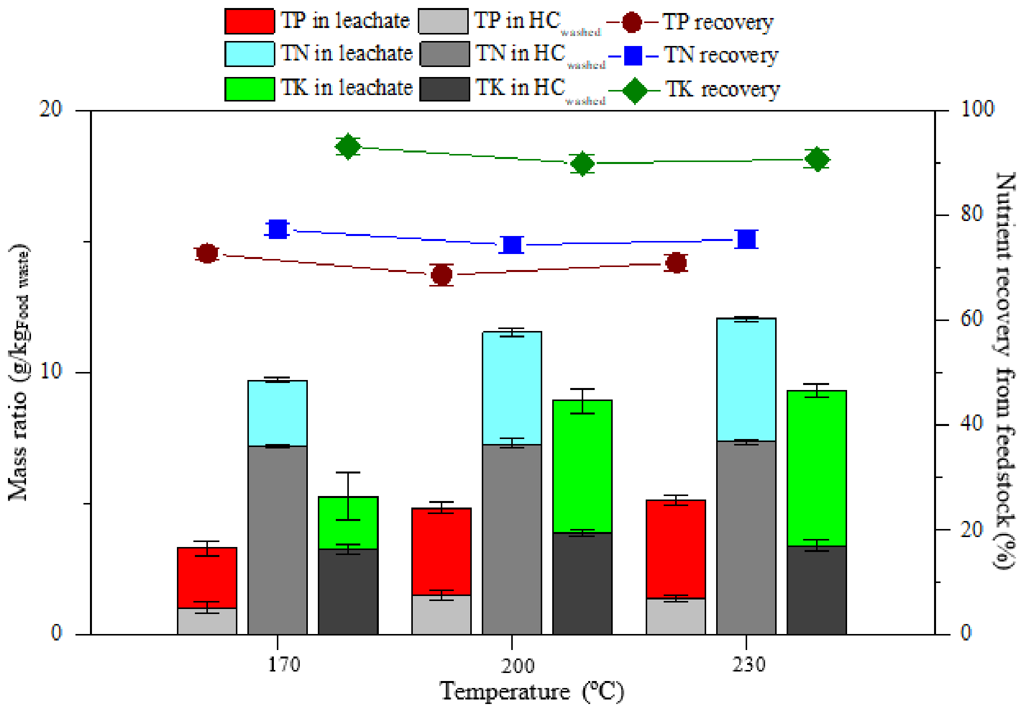

Fig. 1. Total N, P and K distribution after acid washing of hydrochar and nutrient recovery from raw food waste.

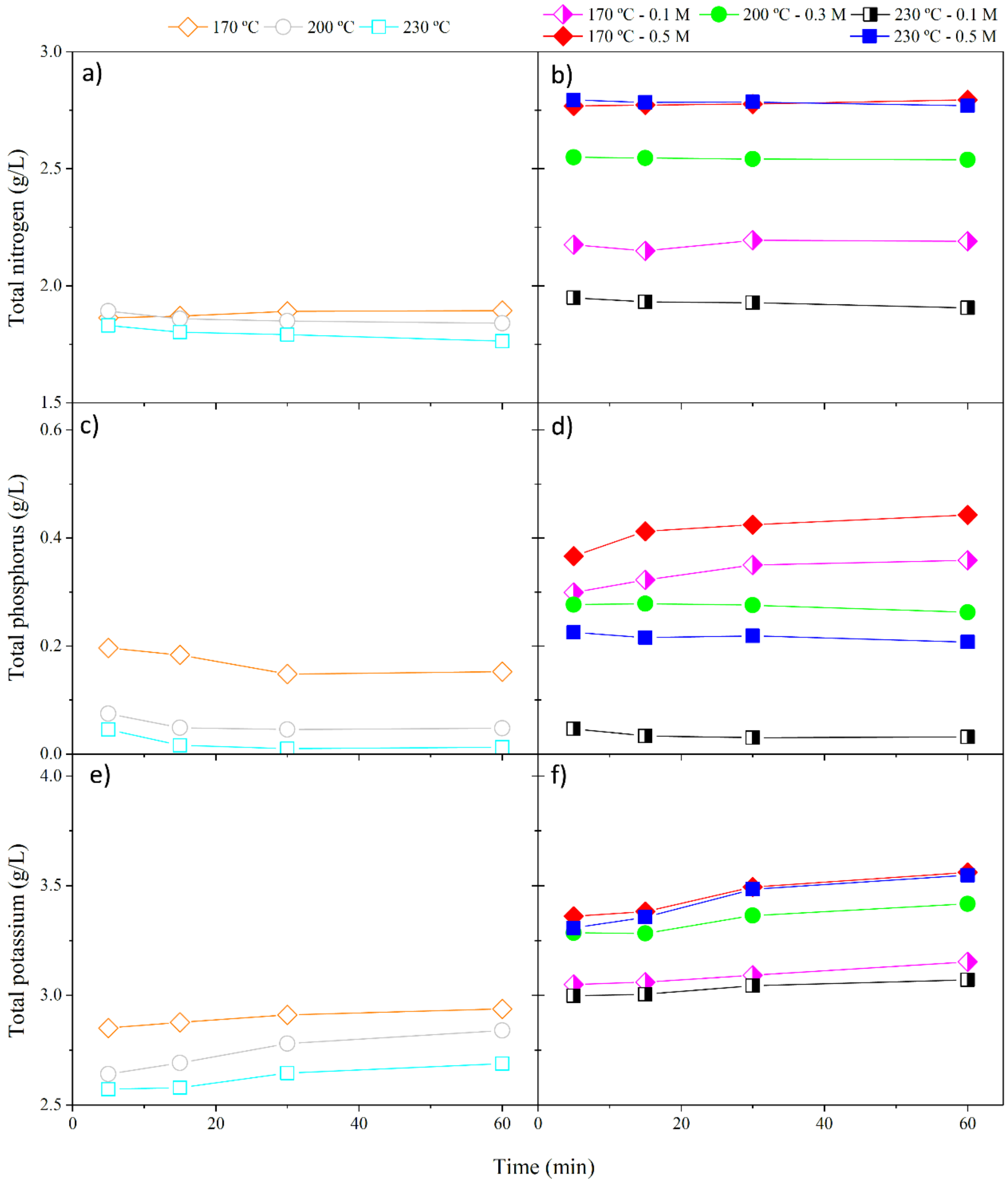

Fig. 2. Time course of phosphorous, nitrogen and potassium in the process water along HTC reaction (a, c and e) and HCl-mediated HTC reaction (b, d and f).

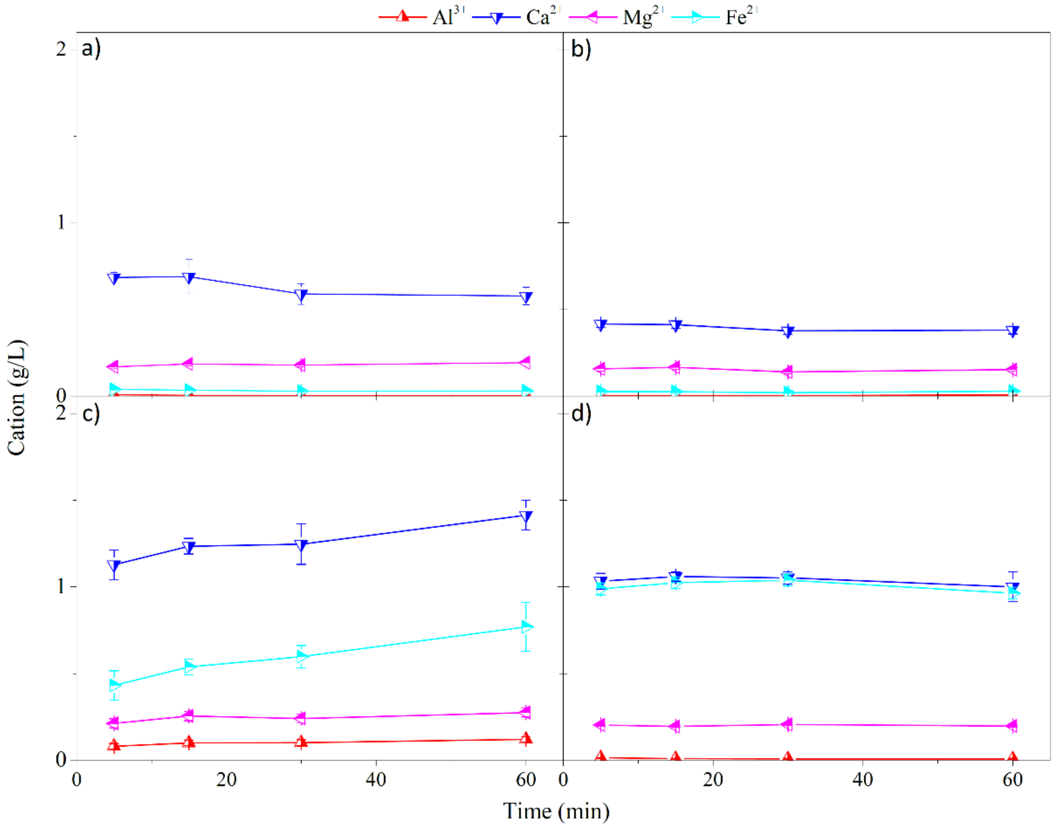

Fig. 3. Time course of the main cations in the process water along HTC carried out at 170 ºC (a), 230 ºC (b), and 0.5 M HCl-mediated HTC at 170 ºC (c), and 230 ºC (d).

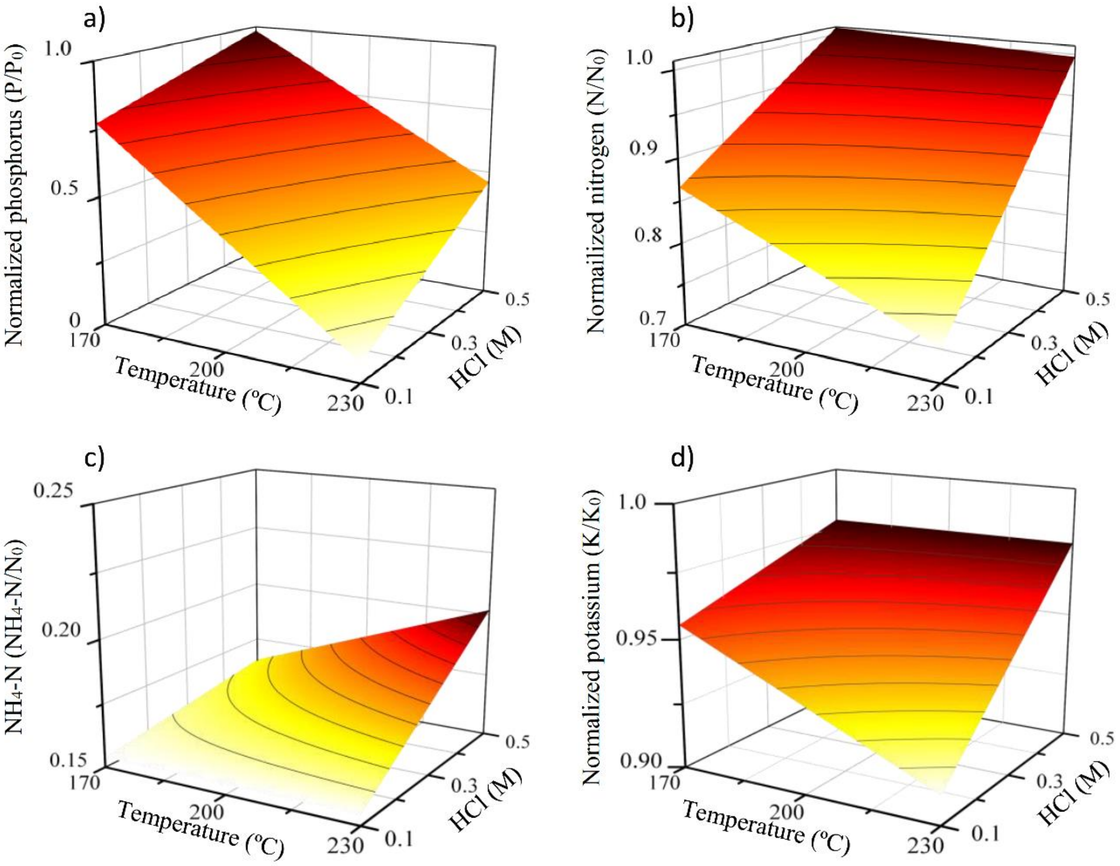

Fig. 4. Response surface of (a) phosphorus (in form of ortho-phosphate), (b) nitrogen, (c) NH_4-N, and (d) potassium recovery in process water at 60 min of HCl-mediated HTC.

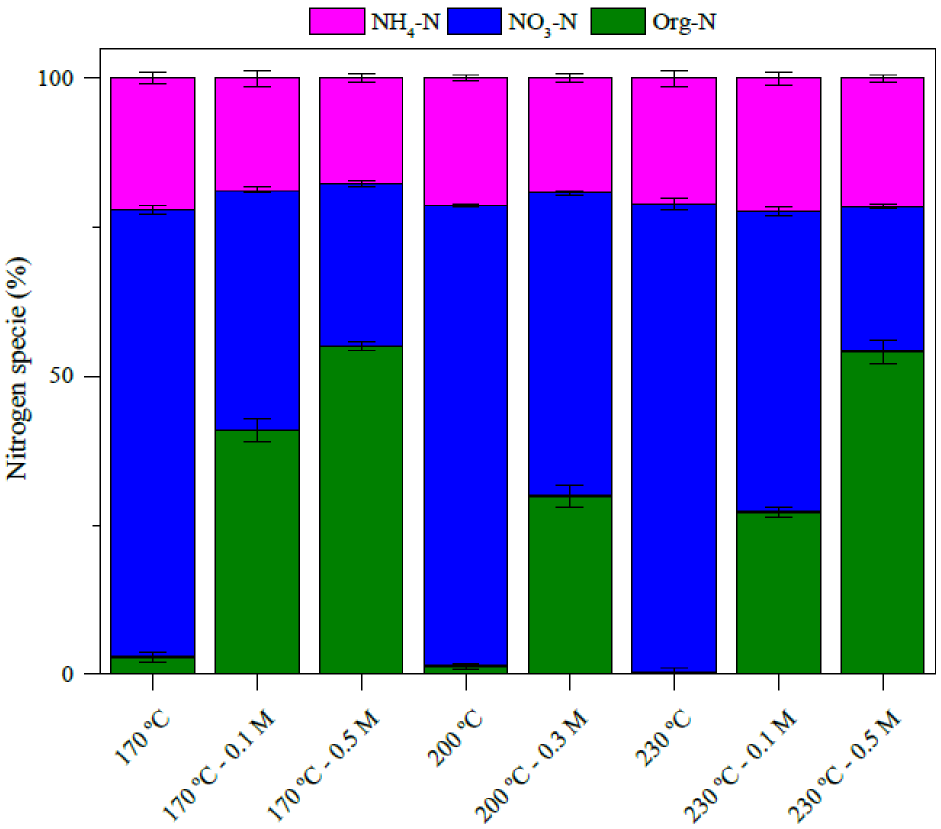

Fig. 5. Distribution of nitrogen species in process water after HTC reaction.