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COD removal of wastewater from hydrothermal carbonization of food waste: Using coagulation combined activated carbon adsorption

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ABSTRACT

Hydrothermal carbonization (HTC) can convert food waste into carbon fuel, thus to provide renewable energy. The wastewater, derived from HTC of food waste, contains complex organic pollutants, with a high COD value and low BOD/COD, which is not feasible for direct anaerobic fermentation. This work studied coagulation combined activated carbon (AC) adsorption to reduce the COD in HTC wastewater to promote its biodegradability. The experimental results indicated that poly aluminum ferric sulphate (PAFS) and polyacrylamide (PAM) are the optimal coagulant and coagulant aid, respectively. With the dosage for PAFS, PAM, and AC was 6 g/L, 10 mg/L, 30 g/L, respectively, it can achieve 68.41% of the COD removal ratio, and promote the transmittance of the wastewater from 23% to 89%. Xarthene, carbamide, ferulic acid and inorganic compounds composed of calcium, magnesium, and aluminum plasma from the sediment were detected by X-ray diffraction analysis (XRD), which proved the synergistic effect between coagulation and AC adsorption. The typical pollutants in HTC wastewater were reduced from 19 to 8 kinds after treatment. BOD/COD ratio also increased from 0.30 in wastewater to 0.75 in liquid residual after treatment, improved for subsequent biochemical treatment. Therefore, the coagulation combined adsorption treatment is thought as a promising method in HTC wastewater pretreatment, and a possible prerequisite in the industrial utilization of food waste HTC technology.

1. Introduction

Increasing biomass energy to replace fossil fuel is effective method for handling the challenge of climate change [1,2]. Hydrothermal carbonization (HTC) can convert wet organic solid waste into high quality carbon fuel, and it has attracted great attention recently [3]. Huge amount of food waste was produced during processing and consumption. It is difficult to be treated, for it contains highly wet components of oil, organic matters, and inorganic salt (moisture 80–90%, NaCl 3– 6%, tec) [4,5]. The HTC method has unparallel characteristics in rapid reaction, utilizations of the products, and low pollution emissions [3]. HTC of food waste would produce the solid and liquid phase, in which the solid phase (hydrochar) can be used for further utilization [6–8]. As for the liquid phase derived from HTC, also defined as HTC wastewater, which contains extensive organic pollutants, N-NH_3^+, Cl^-, and metal ion such as Ca^{2+}, Na^+ [6]. Chemical Oxygen Demand (COD) in HTC wastewater is around 35,000–50,000 mg/L, so HTC wastewater can cause immense contamination, if it is discharged without proper treatment. While its BOD value is only about 10,000–15,000 mg/L, with a BOD/COD ratio of 0.2–0.35, so it is not feasible for direct digestion [6]. Furthermore, it contained phenols, aromatic hydrocarbon, and long chain alkanes, so it is difficult to be treated by simple biochemical method [9,10]. It is essential to develop effective technology of HTC wastewater treatment, promoting the industrial utilization of the food waste HTC technology.

Coagulation is an efficient and economical method to reduce COD in wastewater [11], for it can form flocs to remove the colloids from the wastewater [12]. Coagulant dosage, pH value of the wastewater, temperature, hydraulic condition can significantly influence the efficiency of the coagulation [13,14]. For treating oil-contaminated water, inorganic coagulants polymeric ferric sulfate (PFS), poly aluminum sulfate (PAS), and poly aluminum ferric sulphate (PAFS) have proved to be efficient and economical [14,15]. Organic polymer coagulant, like polyacrylamide (PAM), can enhancing the bridging effect as the coagulant aid in coagulation [16], connect the fine flocs into a larger one [12]. The addition amount of PAM improves the coagulation treatment of oily wastewater with high COD value (5000 mg/L), COD removal ratio can be up to 97% [17–20]. The type and the dosage of the

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coagulant must be carefully considered, because inappropriate coagulant selection and dosage could eventually have awful repercussions on the coagulation effect and even cause the raise of COD value [11,12,21].

Meanwhile, adsorption is also a vital method in high polluted wastewater treatment [22], and the activated carbon (AC) has been widely applied [23]. With a complicated porous structure, AC shows magnificent characteristics in removing organic matters within the wastewater [12,24]. AC adsorption can also be a potential solution in the high polluted wastewater treatment [25–27], COD reduction by AC adsorption can be up to 88% [11]. Alternatively, coagulation combined adsorption is a great option in sewage treatment [24,28]. Combining coagulation bridge effect and the multiple adsorptions of the AC, the process has achieved more significant effect [29–31]. By the addition of PAFS with 120 mg/L (wastewater basis) and AC with 6 g/L, it provided a significant COD remove ratio of 89.27% in the treatment of oily wastewater (original COD value was 5000 mg/L, and the COD value after the treatment was 156.47 mg/L) [24]. Considering its excellent wastewater treatment capacity and low cost [32], the coagulation combined adsorption could be a potential solution in the wastewater treatment with high COD [33,34].

This study aimed to investigate the feasibility of the coagulation combined AC adsorption to remove the COD of the wastewater derived from HTC of food waste, for increasing the BOD/COD ratio, the specific objective of the study includes: i) determination of the optimal dosage for AC adsorption, optimal coagulant type and dosage for coagulation, and optimal ratio of coagulant/adsorbent for coagulation combined adsorption; ii) comparison between different process method and explanation of mechanism; iii) analysis of the residual products from the optimal combination and provide potential utilization or possible guidance for subsequent treatment.

2. Materials and methods

2.1. HTC wastewater and materials

The food waste was collected from a waste treatment center with the capacity of 200 t/d in Hangzhou, China. The moisture content of raw food waste was about 80%. In order to ensure the duplication of experiment and the long period storage of sample, so the food waste sample was dried in an oven (105 °C) and crushed into powder with the particle seize of 0.3–0.4 mm. The characteristics of the food waste were listed in Table 1. The HTC procedure was carried out in a 1200 mL high pressure reactor, adding the food waste powder and deionized water into the reactor at a mass ratio of 1:10. The type of the reactor was HTR-300-7, it was manufactured by Qingdao Changlong Chemical Machinery Corp., Ltd., Qingdao, China. Then the reactor was strictly sealed, and blew pure nitrogen into the reactor furnace to achieve oxygen-free environment. The temperature and pressure of HTC reaction were settled at 250 °C, 4.1 MPa, with a residence time of 30 min. During the whole procedure, the reactor was heated by an electric heater, the electrical heater could achieve 250 °C within 40–45 min, after reaching the predetermined heating time, the reactor was cooled to room temperature. Afterwards, the reaction products were collected, then separated the liquid phase with a vacuum filter which equipping a microporous membrane with the diameter of 0.45 μm. The liquid phase after the filtration was the wastewater of the food waste HTC procedure.

Table 1
Characteristics of the food waste used in the experiments.

Item	Parameter	Value
Proximate analysis (wt%, air-dry basis)	Moisture	2.12
	Ash	11.54
	Volatile matter	72.52
	Fixed carbon	13.82
Ultimate analysis (wt%, air-dry basis)	C	41.58
	H	6.10
	N	2.77
	S	0.16
	O	35.73
Pollutants (mg/L)	Total organic carbon (TOC)	1.074×10^4
	Total nitrogen (TN)	2370

The COD of the process were measure by a spectrophotometer (UV-1100B, Shanghai ZiQi Laboratory Equipment CO., LTD, Shanghai, China), the average value of HTC wastewater was 41,825 mg/L, and the average pH measured by a precision pH meter was 7.34.

The coagulant used in this research, including polymeric ferric sulfate (PFS), poly aluminum sulfate (PAS), poly aluminum ferric sulphate (PAFS), and polyacrylamide (PAM) were purchased from Tengfei Environmental Protection Cor., Ltd., Hangzhou, China. The AC, used as the adsorbent in the research, was purchased from Lv Zhi Yuan Carbon Industry Cor., Ltd., Guangzhou, China.

2.2. COD removal experiments

The COD removal tests were carried out in beakers, containing 50 mL of the wastewater. The operation procedure for AC adsorption and coagulation were listed in Table 2. As shown in Table 2, for AC adsorption, three stages of mixing with magnetic stir would be carried out after the AC were added to the beakers: i) the AC were added into the beakers, they would be rapidly mixed with the wastewater under the stirring speed of 700 r/min for 5 min [35]; ii) switched the stirring speed to 270 r/min, continue the process for 5 min to ensure the complete adsorption and promote the precipitation of the AC [11]; iii) ended up the stirring process and let the beakers stand in for 3 h, as to guarantee all suspended solids had been settled.

As shown in Table 2, for coagulation procedure, three stages of mixing with magnetic stir would be carried out after the coagulants were added to the beakers: i) the coagulant were added into the beakers, set the stirring speed as 600 r/min for 5 min to promote dissolution and coagulation [17]; ii) switch the stirring speed to 240 r/min, continue the process for 5 min to accelerate the formation of flocs [12].

To determine the optimal dosage of AC in AC adsorption, different doses of AC (from 0.2 g/mL to 1 g/mL) were added to beakers in batches, and carried out the AC adsorption stirring procedure in Table 2.

As the pH of the wastewater was 7.34, just in the best application range of coagulant [24,32], the coagulation experiment can be started without adjusting the pH of the wastewater. The coagulation experiments were carried out in two steps: a) different coagulants (PFS, PAS, and PAFS) of the same amount (according to previous pre-test, setting the initial addition amount as 4 g/L) were added to the different beakers, to determine the coagulation with the most significant COD removal ratio for the further test; b) select the ideal coagulant with the best effect, adding different doses of coagulant into the beakers, to determine the best dosing quantity. After the coagulants were added to the beakers, the coagulation stirring procedure was carried out as it shown in Table 2.

The coagulation combined AC adsorption experiments were divided into the three stages. The 1st stage was aim to research the best sequence of the adsorption and coagulation, within the trail, coagulant and adsorbent of the same quantity were added to the wastewater, only changed the sequence of the coagulation and adsorption procedure. Series experiments were taken, including combined adsorption-coagulation method, combined coagulation-adsorption method, and synchronized coagulation-adsorption method. The 2nd stage was settled

Table 2
Operations procedure for AC adsorption and coagulation.

Treating methods	Operation procedure
AC adsorption stirring procedure	Adding AC → 700 r/min stir for 5 min → 270 r/min stir for 5 min
Coagulation stirring procedure	Adding coagulants→600 r/min stir for 5 min → 240 r/min for 5 min

to study the optimum ratio of coagulant and adsorbent, coagulants/adsorbent of different proportions were added to the wastewater. The 3rd stage was designed to effect of coagulant aids (PAM) on COD removal ratio [36], to determine the best ratio of coagulant aids and coagulant under the best proportion of coagulants/adsorbent decided in the previous stage. In each AC adsorption and coagulation procedure, the stirring operation would be carried out after each dosing agent was added, as it was shown in Table 2.

The COD and the pH of liquid samples were measured, then compare to the relevant index of the original wastewater. Generally, use the COD removal ratio as the main index of each trail.

Then select the ideal group with the most significant COD removal ratio, its deposition would be dried and preserved for SEM and XRD analysis to judge its characteristics, its liquid sample would be carried out for FTIR analysis, GC/MS analysis, transmittance measurements (to measure its turbidity), and BOD measurements.

After the stirring procedure in each experiment, the beakers would stand for 3 h. The COD and the pH of different liquid samples were measured, then compare to the relevant index of the original wastewater. Generally, we took the COD removal ratio as the main index in judging the COD removing efficiency of each trail.

Then select the ideal group with the most significant COD removal ratio, collect its deposition and liquid phase and performed the tests mentioned before.

All the trails mentioned before were repeated for 3 times, to avoid the accidental influence and measurement error.

2.3. Analysis method

2.3.1. Liquid sample analysis

The liquid sample analysis mainly consists of COD removal ratio analysis and pH value determination.

The pH value of each sample was measured by a precision pH meter. The COD of the liquid sample from each group were measured by a spectrophotometer, after the sample is oxidized by the digestion agent, their COD values were measured at the wavelength of 630 nm. Generally, the COD removal ratio η_c was used as the main index to determine the COD removal efficiency in each trail, the optimum experiment conditions were also decided by it. The formula of COD removal ratio is Eq. (1):

$$\eta_c = \frac{COD_{original} - COD_{final}}{COD_{original}} \times 100\% \tag{1}$$

To determine the optimal dosage of the AC with highest adsorption efficiency, we use average adsorption efficiency of the AC to evaluate the adsorption efficiency. The formula of average adsorption efficiency is Eq. (2):

$$\eta_{AC} = \frac{COD_{original} - COD_{final}}{dosage} \times 100\% \tag{2}$$

To determine the treating cost in each trail, we comprehensively evaluating the treating efficiency, market price for each dosing agent, and the dosage. Formula Eq. (3) showed the cost for removing every 1000 mg/L COD in 1 L of the HTC wastewater:

$$Removal\ cost = \sum market\ price \times dosage \div \frac{COD_{original} - COD}{1000} \tag{3}$$

The liquid sample from each optimum group in every stage of experiment was measured for BOD analysis and transmittance test by a spectrophotometer. Fourier transformed infrared spectrophotometer (FTIR) were used to identify the chemical bonds within the liquid sample from each optimal group. The liquid sample from each optimal trail were collected, and extracted by n-hexane, then been analyzed by GC/MS system, to determine the components within.

2.3.2. Deposition sample analysis

The deposition from each optimum group in every stage of experiment were dried under 110 °C for 12 h to get solid products.

The dried deposition were examined by X-ray diffraction (XRD, PANalytical X'Pert PRO), aimed to detect the crystal components within. Then Wavelength-Dispersive XRF spectrometer (Thermo Fisher Scientific, ADVANT'X 4200) were used to determine the relative element within the samples. Scanning electron microscopy (SEM) were also used to inspect the compositions of the samples (Fig. 1).

3. Results and discussions

3.1. Adsorption effect of AC

Fig. 2 displayed the COD removal ratio and the average COD removal efficiency (with same AC dose) by AC adsorption, from 20 g/L to 100 g/L of AC dosage, also marked the COD values of the liquid sample from different groups. It could be observed that the COD removal ratio rising as the increasing dosage of AC. It can be observed the group with the adsorbent addition amount of 30 g/L (COD removal ratio is 28.48%) had the most significant COD removal efficiency compared to the other trails. The findings were consistent with the previous work [25–27,35,37,38].

After adsorption and precipitation process, obvious stratification can be witnessed, most AC depositions at the bottom of the beakers and the liquid phase of each group are relatively clear compared to the original wastewater, the transmittance of the liquid sample after the treatment was promoted to 68% from 23%.

The following experiments chose 30 g/L as the optimal addition amount for the AC adsorption, for the AC adsorption had the highest COD removal efficiency with this dosage, and could also improve the economy of the whole process.

3.2. Coagulation effect

3.2.1. Determination of the optimal coagulant

In order to facilitate the follow-up tests, it is necessary to select the ideal coagulant. In Table 3, The COD removal ratio of three coagulants, including PAS, PFS, and PAFS, were displayed. With the same dosage of 2 g/L, PFS has the maximum COD removal ratio (14.94%), followed by PAFS (13.45%), while PAS proved to have little effect in this trail. After the coagulation process with PFS, the liquid sample appeared to be darker and had smaller flocs settled on the bottom of the beaker compared to other groups, and the transmittance of the liquid sample was lower. This phenomenon also was indicated by Lee [18], for the iron ion have reactions with colored colloids within the wastewater, then the liquid sample appeared dark color with the dissolved matter generated by the process [39–41]. Considering this characteristic of the PFS, aimed to achieve better coagulation effect with low cost [42,43] and clearer liquid phase, PAFS was chose as the ideal coagulant for the following experiment.

3.2.2. Determination of the optimal dosage of PAFS

The following experiments discussed different PAFS addition amount, focused on the investigation towards the optimal PAFS dosage. The specific data and results of the experiments are shown in the Fig. 3. Compared to the curves drawn with the COD removal ratio in the previous AC adsorption experiment, this COD removal curve showed an evident peak. The removal ratio continuously increased as the PAFS addition amount increases till 6 g/L, the highest removal ratio with 26% is reached. After that, the coagulation effect gradually becomes worse with the increase of coagulants. While add PAFS to the wastewater as the amount of 10 g/L, the COD value of the liquid sample in this group was even slightly higher than the original wastewater before the coagulation procedure.

This observation demonstrated the thesis about the coagulation

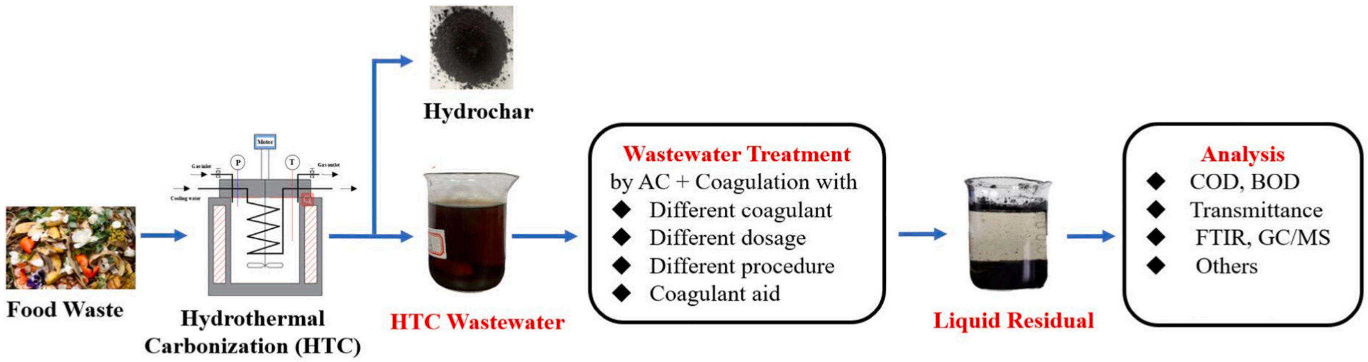

Fig. 1. Flow chart of experimental work.

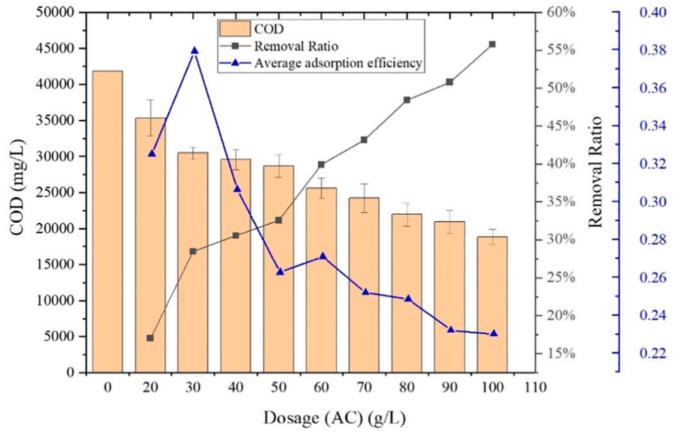

Fig. 2. COD values, removal ratio, and COD removal efficiency of AC adsorption.

Table 3
Market price, COD value of the liquid sample and COD removal ratio of different coagulants[a].

Coagulants[b]	PAS	PFS	PAFS
COD (mg/L)	41,200	35,575	36,200
COD Removal Ratio (%)	1.49	14.94	13.45
Transmittance[c] (%)	25	28	33
Market cost (RMB/kg)	2.37	2.62	2.49
Removal cost (RMB/g)	0.00758	0.00909	0.00875

[a] COD of original wastewater: 41825 mg/L.
[b] 2 g/L dosage.
[c] Transmittance of original waste water: 23%.

mechanism mentioned in the other works [24,39,44]. With the uneven distributions of the hetero-charges, certain electrostatic attraction was created between particular organic particles within the wastewater, causing the zeta potential unequal to zero, in such way as to form the flocs between the colloids [36]. With various addition amount of the coagulation, the zeta potential could various between a certain range, within the range, the coagulation can provide satisfying coagulation effect, a large amount of the colloids changed into flocs and finally become solid sediment and separated from the wastewater, then the COD value of the wastewater is reduced [11]; this phenomenon is also described as the Coagulation Window. The peak of the COD removal curve (6 g/L), represented the optimal condition in the coagulation treatment of the HTC wastewater, and 4 g/L ~ 8 g/L formed an ideal coagulation window. Outside this range, with excess coagulant addition amount, the colloidal destabilization occurs and affected the coagulation effect, leads to the reduction of COD removal ratio. While adding much more coagulants(10 g/L), due to the strong solubility of PAFS, the excess Fe^{3+}, Al^{3+}, and SO_4^{2-} contained by the PAFS become part of solute in the wastewater, which can trigger the colloidal re-stabilization, the original colloid with negative charge in water is changed into colloid with positive charge, re-stabilize the colloid and avoid the sediment of the colloids and finally cause the repercussion that the COD removal effect of the liquid samples in this group (10 g/L) is even weakened.

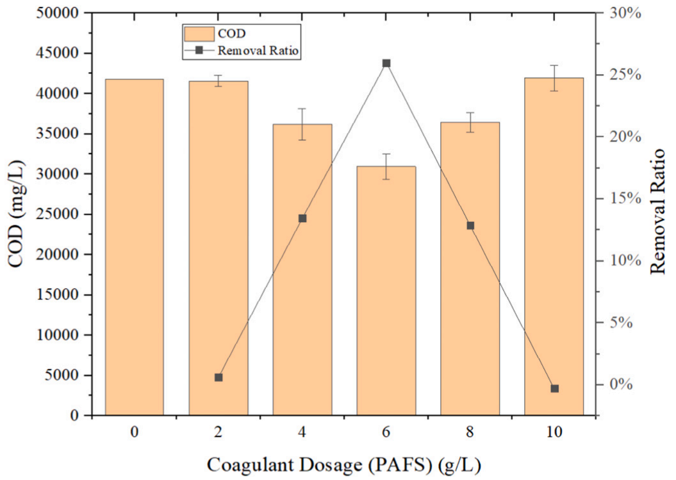

Fig. 3. COD values and removal ratio of PAFS coagulation.

Comparing to the original wastewater, the transmittance of liquid sample treated by PAFS at a dosage of 6 g/L was promoted to 39% after coagulation from 23%.

After the comprehensive considerations on the selection of optimal coagulants and best dosage, take COD removal ratio as the main factor in the evaluation of the coagulation effect, it is prudence to think that the PAFS is the optimal coagulant in the coagulation treatment of the wastewater, and the ultimate ideal dosage is 6 g/L. Furthermore, the following trails would select the PAFS in every coagulation procedure.

Table 4
The COD values and the COD removal ratio of different treating methods[a].

Methods	CAC	CCA	SCA
COD (mg/L)	36,325	23,825	26,200
COD Removal ratio (%)	14.68	44.04	38.46
Removal cost (RMB/g)	0.0355	0.1252	0.01808

[a] COD of original wastewater: 41825 mg/L.

3.3. *Effect of coagulation combined AC adsorption*

3.3.1. *Discussion about ideal processing sequence*

Table 4 displayed the COD values and the COD removal ratio from different trail groups, which had been processed by various processing sequence, including combined adsorption-coagulation (CAC) method, combined coagulation-adsorption method (CCA), and synchronized coagulation-adsorption (SCA) method. As is mentioned in the previous coagulation analysis, PAFS was chose as the target coagulant, and the addition amount was 6 g/L, the addition amount of the AC was 30 g/L. Compared with the other two process methods, the CAC method had a poor performance on the COD removal ratio (only 14.68%). Alternatively, the CFC method and the SCA shared a similar performance on the COD removal ratio, while CCA method still had a slightly better COD removing efficiency than SCA method.

Hence, the findings clearly demonstrated the hypothesis on the synergistic effect in the coagulation combined AC adsorption [36,45]. While the coagulation process removed the organic macromolecules through forming flocs which insoluble in wastewater and became depositions, the AC mainly adsorbed the organic micro molecules with its porous structure, therefore the COD value of the wastewater decreased as the organic matters within had been reduced [45]. In SCA method, porous structure promoted the contract area between the coagulant and the wastewater, reduced the compliance within the process, and provided structures for the formation of the flocs [36], thus achieved a better effect than flocculent and the adsorbent acted separately. As for the CAF method, this synergistic effect performed a weaker coordination compared the SFA method, the interval between the adsorption and coagulation procedure reduced this auxiliary effect, which decisively displayed an unsatisfying repercussion [37,46,47]. The CCA method displayed another type of synergy effect, through forming floc grids, coagulants triggered the sweeping effect within the reaction, which accelerated the formation of flocs with larger size [37]. Also, the addition of the coagulation changed the density of the wastewater and strength the netting mechanism [24], combined with the advantages all above, promoted the adsorption and sediment effect of the AC adsorption procedure, which eventually provided much better treating effect than the individual procedure of the coagulation and adsorption. It can therefore be inferred that combined coagulation-adsorption method, which literally means using AC adsorption after the coagulation, is the optimal method in the COD removal of wastewater, hence we have chosen this method in the following trails.

3.3.2. *Discussion about optimal ratio of coagulant to adsorbent*

Fig. 4 displayed the COD values and the COD removal ratio of various trails, while fixing the addition amount of AC as 30 g/L, the ratios of coagulant to absorbent by adding PAFS with various quantities were changed. Taking the quantity of PAFS as X-axis coordinate, a significant peak on the COD removal ratio curve can be observed. While the PAFS dosage is below 6 g/L, the COD of the liquid samples reduced as the dosage raises, then reach the peak at around 6 g/L and achieve the maximum COD removal ratio of 44.04%. Afterwards, when the addition amount is in the range of 6–12 g/L, the COD removal ratio decreased as the dosage of PAFS increased. In the view of the ratio of coagulant to adsorbent, when the PAFS dosage was 6 g/L and the AC dosage was 30 g/L, the coagulation combined AC adsorption had the highest COD removal ratio, which means the optimal ratio of PAFS to AC is 0.2.

The data strongly demonstrated the previous thesis on the synergistic effect in the coagulation combined AC adsorption, by enhancing the netting mechanism and sweeping effect by forming flocs, the adsorption efficiency was promoted. As for the negative correlation of the COD removal ratio and the PAFS addition amount in the range of 6–12 g/L, the fact perfectly accords with the coagulation window thesis. As the excess coagulant had been added into the wastewater, the excess inorganic salt ion from the coagulant could become part of solute in the wastewater [23], which can trigger the colloidal re-stabilization. Then, the original colloid with negative charge in water is changed into colloid with positive charge, re-stabilize the colloid and avoid the sediment of the colloids, and eventually led to this repercussion.

The transmittance of the liquid sample after the treatment was promoted to 79% after treated by the coagulation combined adsorption in optimal dosage (6 g/L, 30 g/L).

Took prudence attitude towards the statistics from the previous experiments and considered the current findings, comprehensively evaluating economy, treating efficiency, and sustainability, we chose 0.2 as the optimal ratio of the coagulant and absorbent for the following trails, which means the dosage for the PAFS and AC was 6 g/L and 30 g/L.

3.3.3. *Research on optimal dosage of coagulant aid*

PAM was used as the coagulant aid and adjusted the ratio between PAM and PAFS by changing the addition amount of PAM. Fig. 5 provided vivid results of the trail groups in the experiment on deciding the optimal dosage of the coagulant aid. Based on the previous experiments, the dosage of the PAFS and AC were fixed as 6 g/L and 30 g/L, which had the optimal ratio of coagulant to adsorbent, and changing the addition amount of PAM. The COD value of the liquid samples from each trail groups were measured, then drew the COD removal curve with the preset evaluation formula. Within the figure, a significant peak on the COD removal ratio can be observed, as the PAM addition amount was 10 mg/L, the removal ratio reached 68.41%, which is far better than any

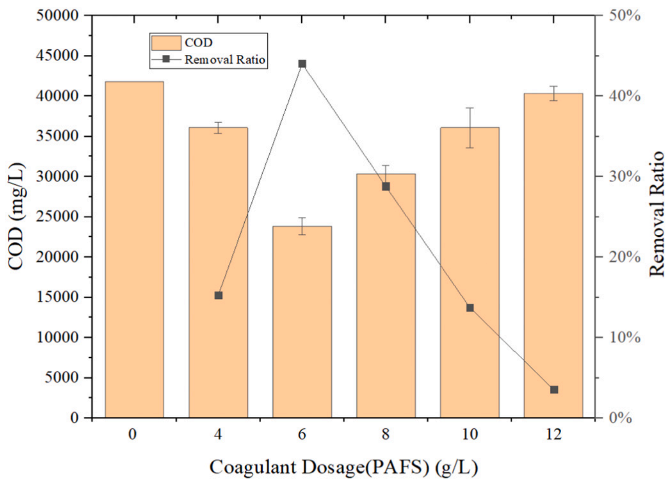

Fig. 4. COD values and removal ratio of PAFS coagulation combined AC adsorption (30 g/L).

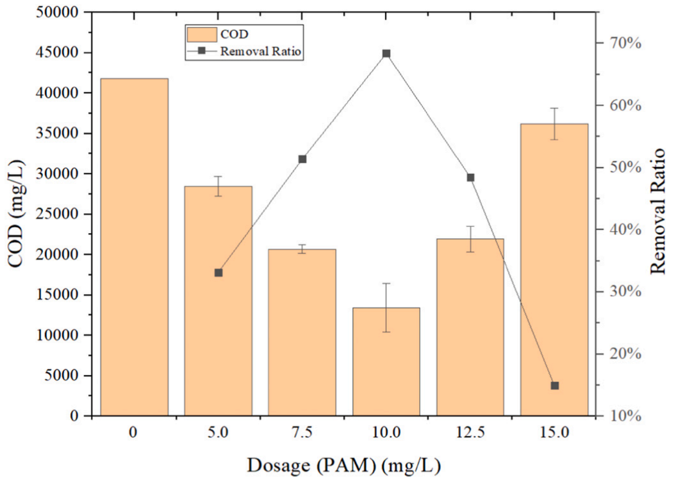

Fig. 5. COD values and removal ratio of various PAM addition.

other previous treating sequence.

The results perfectly demonstrated with the previous thesis, while using PAM as coagulant aid for PAFS in coagulation, the long chain organic macromolecules within PAM promoted the sweeping and bridging effect. With the uneven distributions of the hetero-charges, certain electrostatic attraction was created between particular organic particles within the wastewater, causing the zeta potential unequal to zero, in such way as to form more flocs between the colloids and accelerated the coagulation process [36]. With various addition amount of the coagulant aid, the zeta potential could various between a certain range, within the range, the coagulant aid has a strong promoting effect on the coagulation process; when excess coagulant was added in the wastewater, it would affect the electric neutralization, and the colloidal destabilization occurs, thus the bridging and sweeping effect continuously weakened [40,48–51]. As for the adsorption procedure, coagulant aid enhanced the netting mechanism and sweeping effect by forming flocs [46], hence the adsorption efficiency was promoted.

Appendix (a)(b) presented vivified results of the wastewater treated with different addition amount of the coagulant aid, it can be clearly observed the excellent effect after the coagulation combined adsorption. In the view of whole picture, the addition of PAM significantly enhanced the precipitation, the liquid samples had clearer appearance compared to other procedures. The transmittance of the liquid sample after the treatment was promoted to 89% from 23%.

Considering various implications indicated in the current findings, comprehensively evaluating economy, treating efficiency, and sustainability, at the end of day, it can be assumed that 10 mg/L is the ideal dosage for the PAM in the coagulation combined AC adsorption, the optimal dosage for PAFS, PAM, and AC was 6 g/L, 10 mg/L, 30 g/L, which can achieve a removal ratio of 68.41% in the wastewater (original COD value is 41,825) from food waste HTC.

3.4. *Analysis of the deposition from the optimal group*

3.4.1. *XRD analysis*

Fig. 6 displayed the XRD patterns of the depositions from every optimal group. Fig. 6(a) represented the XRD patterns for the deposition collected from the AC adsorption, it can be uncovered the spectrum that the main components adsorbed by the AC were trioxane, amino, and inorganic compounds composed of calcium, magnesium, and aluminum plasma. Fig. 6(b) represented the XRD patterns for the deposition collected from the PAFS coagulation, which was mainly consists of anthrone, ferulic acid, and compounds calcium through forming flocs. Fig. 6(c) presented the XRD patterns for the PAFS combined AC adsorption process, xarthene, carbamide, ferulic acid and inorganic compounds composed of calcium, magnesium, and aluminum plasma were detected from the sediment. Fig. 6(d) presented the XRD patterns for coagulant aided coagulation combined adsorption process, xarthene, troxane, ferulic acid and inorganic compounds composed of calcium, magnesium, and aluminum plasma were detected from the sediment.

These findings clearly demonstrated the previous results [7,32,52]. The AC adsorption and coagulation procedure removed various organic pollutants in the wastewater by different mechanisms [53]. When treating the wastewater with coagulation combined adsorption procedure, which trigger synergy effect, through forming floc grids, coagulants triggered the sweeping effect within the reaction, then

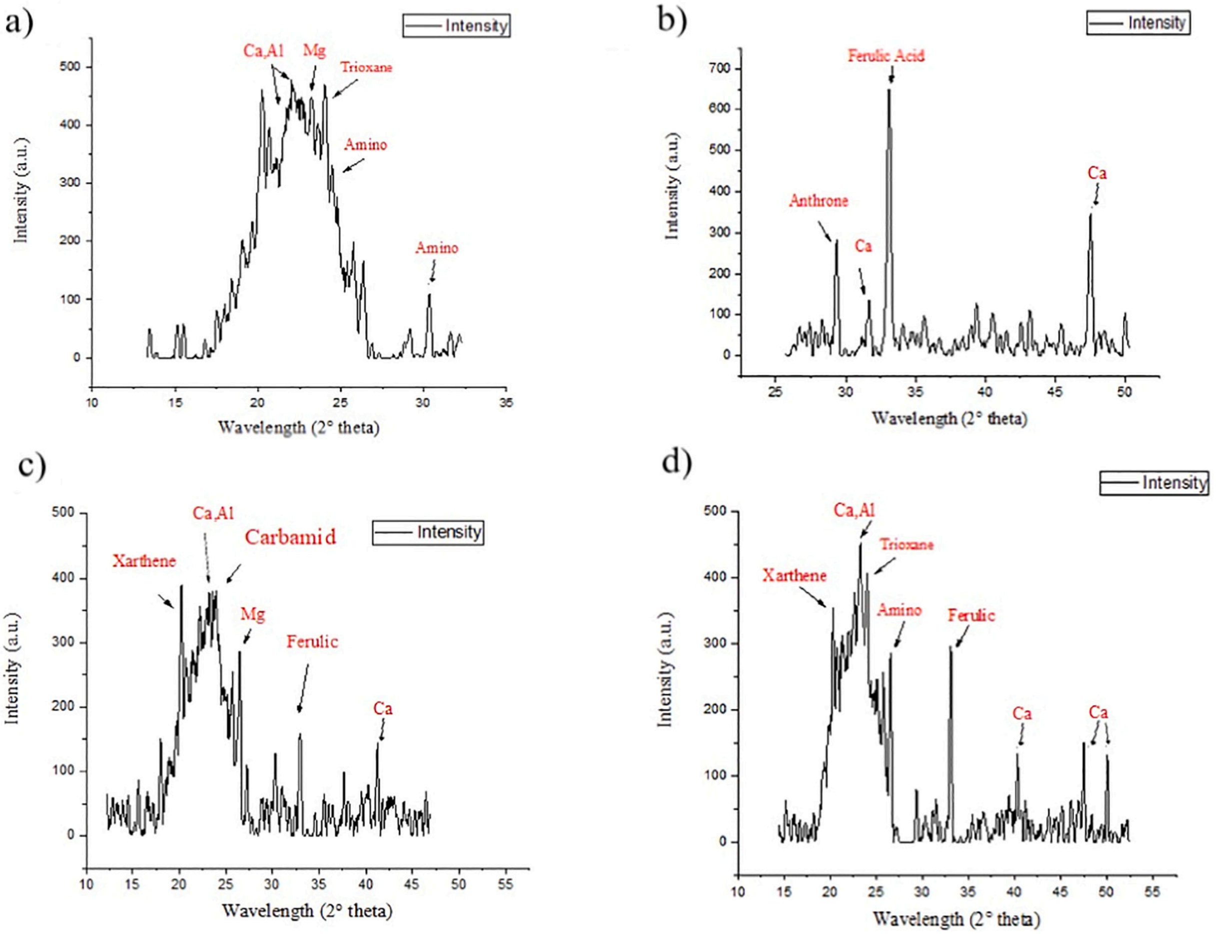

Fig. 6. XRD patterns for sediments from different treatments (a) AC adsorption; (b) PAFS coagulation; (c) PAFS coagulation combined adsorption; (d) PAFS+PAM combined adsorption.

accelerated the formation of flocs, hence more organic and inorganic pollutants has been detected from the sediment. As it was shown in Fig. 6 (d), with the bridging effect of the coagulant aid, more organic and inorganic pollutants were fixed within the deposition, demonstrated the coagulant aided coagulation combined AC adsorption has the highest COD removal ratio.

3.4.2. SEM patterns

Fig. 7 provided SEM images of the sediments collected from each optimal trail, from low magnification images, it could be easily observed that the AC was the main content displayed in the figure. In high magnification images, the micropores on the surfaces of the AC could be clearly observed, which demonstrated that the high adsorption ability was caused by its high specific surface and extensively micropore structure [11,24].

Compared to Fig. 7(a), the micropores of the AC from Fig. 7(b)(c) adsorbed much more surface groups, the findings further demonstrated the synergy effect in coagulation combined AC adsorption, through forming floc grids, coagulants triggered the sweeping effect within the reaction, which accelerated the formation of flocs with larger size.

3.5. Analysis of the liquid sample from optimal group

3.5.1. Functional group analysis by FTIR

The FTIR analysis uncovered the chemical bonds within the original HTC wastewater, and the liquid samples after all optimal treating methods. In Fig. 8(a), the miscellaneous peak between 4000–3500 cm^{-1} demonstrated the existence of water within the original HTC wastewater, the patterns between 2000–2200 cm^{-1} stood for the overtone spectrum for aromatic hydrocarbon. The peak between 1400–1300 cm^{-1} demonstrated the existence of C—H groups. In Fig. 8(a)–(d) the peak between 3000–3400 cm^{-1} represented the stretching vibration of hydroxyl, the curve between 2500 and 3000 cm^{-1} represented for the existence of methylene [54]. And the peak between 1500–1650 cm^{-1} gave significant reflection on the existence of C=C structure and aromatic rings [55].

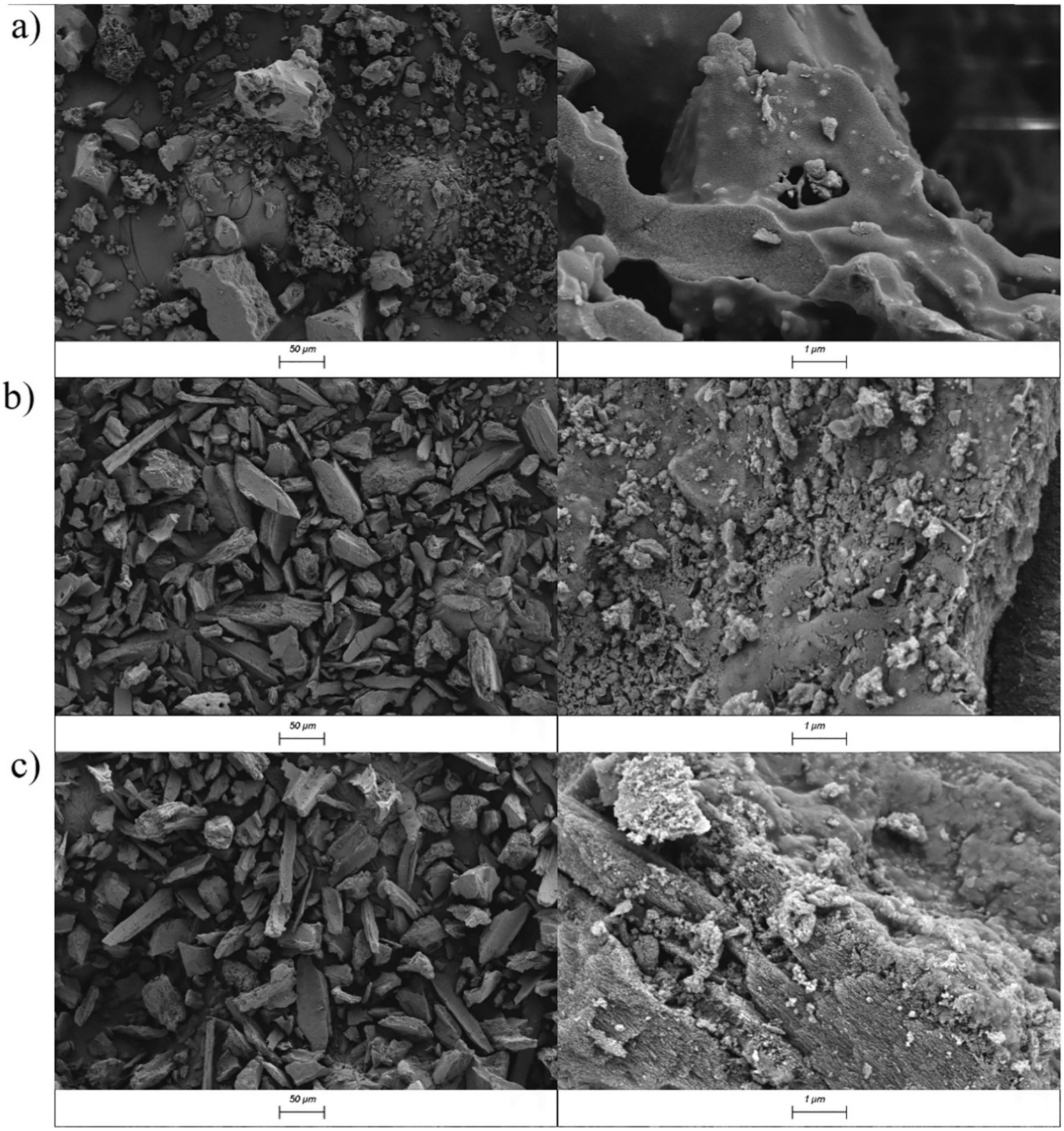

Fig. 7. SEM images of sediments from different treatments: (a) AC adsorption; (b) coagulation combined AC adsorption; (c) coagulation combined AC adsorption with coagulant aid.

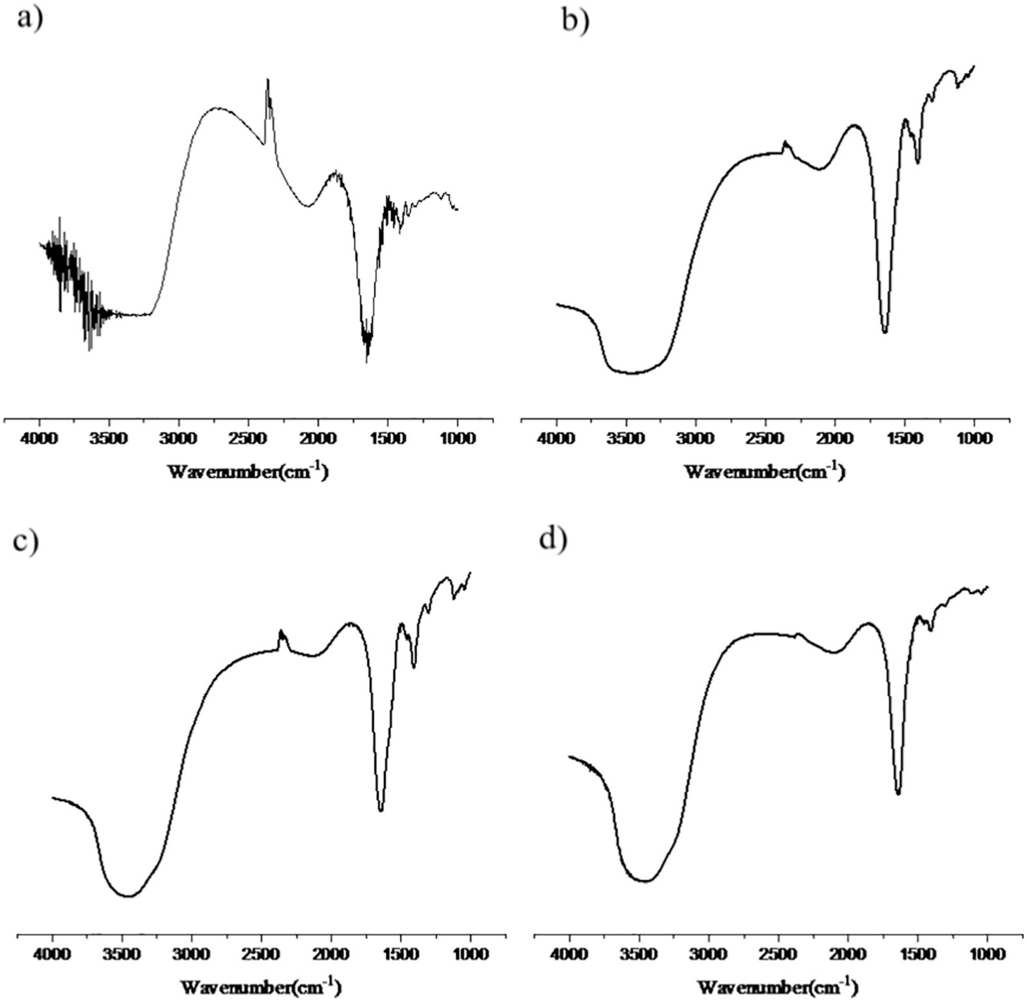

Fig. 8. FTIR images of liquid residuals from different treatments: (a) Original HTC wastewater; (b) AC adsorption; (c) PAFS coagulation combined AC adsorption; (d) PAM, PAFS coagulation combined AC adsorption.

The following findings clearly demonstrated the previous results, while the pretreatment cannot remove COD, which means there remained some pollutants within water. Further discussion on GC/MS analysis would gave more specific results on the organic pollutants removed within the process.

3.5.2. *Organic compound analysis by GC/MS*

The original wastewater and the liquid samples collected from various trails were measured by GC/MS, and the results are listed in Fig. 9. The comparisons of different treating methods with the original HTC wastewater were shown in Fig. 9(a)–(c), and the ion current of all treating methods was displayed in Fig. 9(d). The original HTC wastewater, contained a great number of organic pollutants, and the typical pollutants within the HTC wastewater were listed in Table 5, roughly contained 19 typical organic pollutants, including phenols, hydrocarbons, esters, and amines [56]. The result displayed in GC/MS ion current figures was consistent with the results shown in FTIR analysis, the organic pollutants detected in the liquid phase contained complex organic macromolecules, which had a long molecular chain.

As it is shown in Fig. 9(a), the AC adsorption could have a significant removal effect on the phenols, alkanes, and esters, and the number of the typical pollutants reduced to 10 kinds. And the adsorption procedure also had a significant removal effect on long chain macromolecules, like C26-C30 alkanes. The findings demonstrated the fact that the adsorption capacity of AC was determined by the surface properties, molecule characteristics, competitions between different components, and particle structure [24], while GC/MS images uncovered the high content of the phenols and alkanes. The phenols and some alkanes detected and listed in Table 5, could be easily been adsorbed by the AC, since their diameters were smaller than the pore size of the AC, thus they could easily enter the inside body of the AC. The π- π hypothesis focus on the π-π dispersion interaction [57], the certain reactions were taken place between the π electron between aromatic rings and activated partial graphite layers [23,45,57]. As for long chain macromolecule alkanes, the adsorption procedure seemed to have a weaker effect, for the diameters of those alkanes were larger than the pore size of the AC and limited the adsorption effect. But the adsorption procedure could have a better adsorption effect on the long chain alkanes with higher molecular weight, for the intermolecular van der Waals force raised as the molecular weight raised [58,59].In this way, the AC adsorption could have a significant COD removal effect on HTC wastewater.

The Fig. 9(b) provided the total ion current image of coagulation combined AC adsorption procedure. Compared to Fig. 9(a), the coagulation procedure could greatly improve the removal effect on the long chain macromolecules, like C21 ~ C30 alkanes, also reduced the contents of phenols within the liquid samples. Hence, the number of the typical pollutants were decreased to 9 kinds. The long chain macromolecule alkanes, which could trigger the sweep effect and been removed by forming floc in the coagulation procedure [60], were removed for about 43% within the process. As in Fig. 9(c), with the addition of coagulant aid, the long chain organic macromolecules within PAM promoted the sweeping and bridging effect. With the uneven

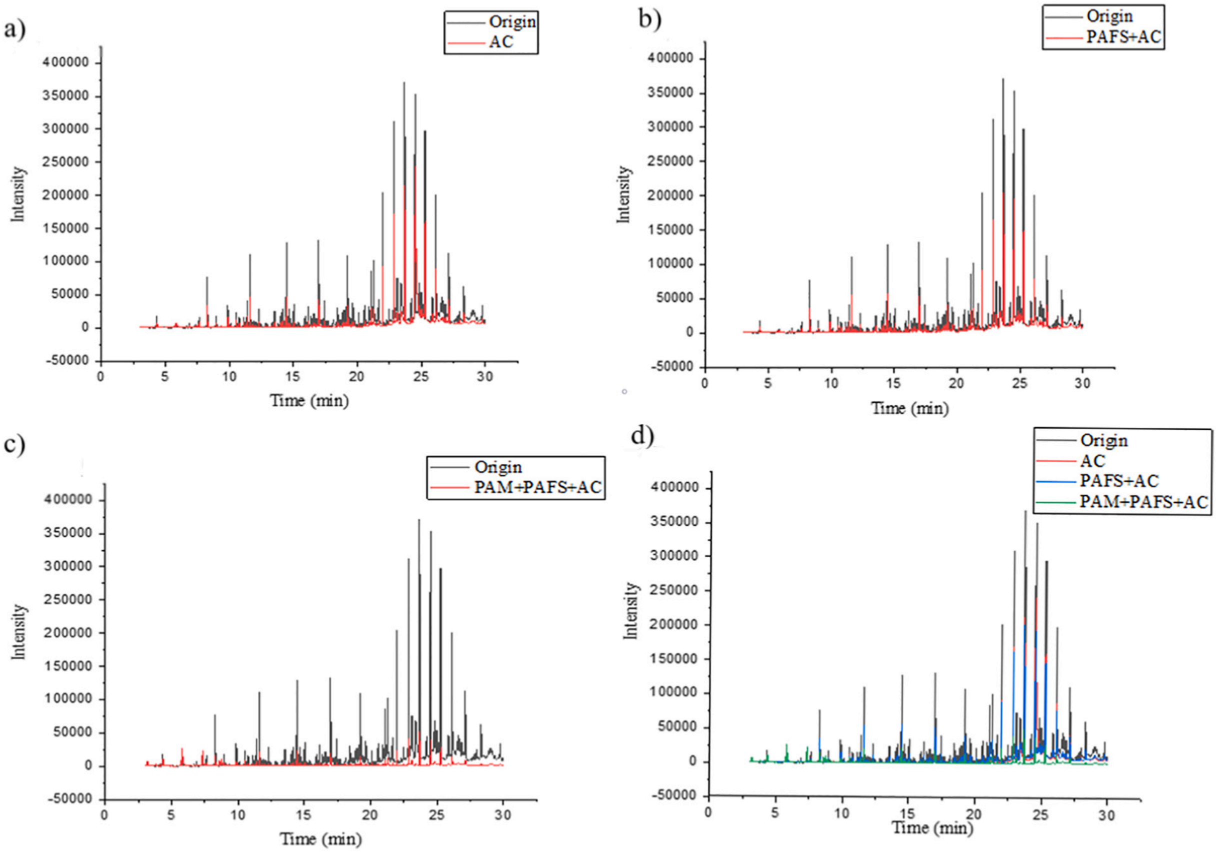

Fig. 9. GC/MS comparison among different treatments and original wastewater: (a) AC adsorption; (b) PAFS coagulation combined AC adsorption; (c) PAM, PAFS coagulation combined AC adsorption; (d) all of the treatment methods.

Table 5
Typical pollutants in liquid samples.

Treating methods	Typical organic pollutants (percentage of detected pollutants)
Original wastewater	1H-Pyrrole,1-methyl-C_5H_7N (0.105%); 1H-Pyrrole, 3-methyl-C_5H_7N (0.086%); Disulfide, dimethyl $C_2H_6S_2$ (0.067%); 1H-Pyrrole, 2-ethyl-C_6H_9N (0.0473%); Phenol, C_6H_5OH (0.053%); Pyrazine, methyl-$C_5H_6N_2$ (0.162%); 4- methyl phenol, C_7H_8O (0.009%); 2,5 – dimethylphenol, $C_8H_{10}O$(0.007%); Naphthalene, $C_{10}H_8$ (0.026%); Acenaphthylene, $C_{12}H_{10}$ (0.041%); Sodium nitrate, $NaNO_3$ (0.431%); Heneicosane, $C_{21}H_{44}$ (0.154%); Docosane, $C_{22}H_{46}$ (0.597%); Tricosane, $C_{23}H_{48}$(0.856%); Tetracosane, $C_{24}H_{50}$(1.060%); Triacontane, $C_{30}H_{62}$ (0.935%); Hexacosane, $C_{26}H_{54}$ (0.600%); Octacosane, $C_{28}H_{58}$ (0.285%); Nonacosane, $C_{29}H_{60}$ (0.150%);
AC	1H-Pyrrole, 1-methyl-C_5H_7N (0.006%); Heneicosane, $C_{21}H_{44}$ (0.492%); Docosane, $C_{22}H_{46}$ (0.919%); Tricosane, $C_{23}H_{48}$ (0.919%); Tetracosane, $C_{24}H_{50}$ (1.187%); Triacontane, $C_{30}H_{62}$ (1.285%); Phenol, C_6H_5OH (0.044%); Hexacosane, $C_{26}H_{54}$ (0.580%); Octacosane, $C_{28}H_{58}$ (0.288%); Nonacosane $C_{29}H_{60}$ (0.587%);
PAFS+AC	Heneicosane, $C_{21}H_{44}$ (0.141%); Docosane, $C_{22}H_{46}$ (0.494%); Tricosane, $C_{23}H_{48}$ (0.855%); Tetracosane, $C_{24}H_{50}$ (1.041%); Phenol, C_6H_5OH (0.351%); Hexacosane, $C_{26}H_{54}$ (0.544%); Octacosane, $C_{28}H_{58}$ (0.212%); Nonacosane $C_{29}H_{60}$ (0.188%); Triacontane, $C_{30}H_{62}$ (0.712%);
PAM+PAFS+AC	Heneicosane, $C_{21}H_{44}$ (0.120%); Docosane, $C_{22}H_{46}$ (0.365%); Tricosane, $C_{23}H_{48}$ (0.630%); Tetracosane, $C_{24}H_{50}$ (0.784%); Triacontane, $C_{30}H_{62}$ (0.600%); Hexacosane, $C_{26}H_{54}$ (0.394%); Octacosane, $C_{28}H_{58}$ (0.143%); Nonacosane $C_{29}H_{60}$ (0.076%);

distributions of the hetero-charges, certain electrostatic attraction was created between particular organic particles within the wastewater, causing the zeta potential unequal to zero, in such way as to form more flocs between the colloids and accelerated the coagulation process [36]. In this mechanism, the long chain alkanes and phenols were removed by forming flocs, thus the typical pollutants were reduced to 8 kinds. The findings clearly demonstrated that the coagulation combined AC adsorption, and PAM aided coagulation combined AC adsorption could have a significant COD removal effect on HTC wastewater, while more than 70% of long chain alkanes and most of the phenols were removed. The increase of the intensity between 5– 7.5 min was caused by the deposition of PAM in the solution, and turned into acrylamide [54], which could promote the biodegradability of the wastewater, for the acrylamide was easy to be composed by the microorganisms.

3.5.3. BOD analysis of the liquid sample from the optimal groups

Table 6 displayed the BOD values and BOD/COD ratio of the liquid sample from the optimal groups. The BOD/COD ratio generally reflects the biochemical index of the samples, which provides vital references for the following biochemical treatment of the samples. Studies had proved that when the BOD/COD ratio is between 0.3–0.5, so the current water will be suitable for anaerobic fermentation treatment [45]. As the BOD/

Table 6
The COD, BOD values of the optimal groups.

Methods	AC	PAFS + AC	PAM + PAFS + AC	Original wastewater
COD (mg/L)	30,450	23,825	13,450	41,825
BOD (mg/L)	11,380	10,760	10,100	12,400
BOD/COD ratio	0.373	0.451	0.750	0.296

COD ratio is over 0.5, the liquid samples would be typically suitable for biochemical treatment.

As it is showed in Table 6, the AC adsorption process approximately raised the BOD/COD ratio for 0.077 compared to the original wastewater, which greatly promoted the potential for further biochemical treatment. Comprehensively considering the conclusions in GC/MS and FTIR analysis, the adsorption procedure reduced the phenols, aromatic hydrocarbon, and certain long chain alkanes, which could be harmful for the aerobic fermentation, and eventually promote the biodegradability of the wastewater. Those refractory organics had a BOD/COD ratio at around 0.03–0.17 [61–63], the coagulation and adsorption procedure had been demonstrated to significantly remove those refractory organics, which explained that the decrease of BOD was less than the decrease of COD.

The PAFS coagulation combined AC adsorption further raised the BOD/COD ratio for 0.155, achieved 0.451, by removing inorganic compounds and organic matter within the liquid samples through forming flocs and adsorption, hence the wastewater was clearly suitable for biochemical treatment after this procedure. With the addition of PAM, the BOD/COD ratio raised to 0.750, it could be inferred from the GC/MS and FTIR results, that the addition of this organic coagulant greatly removed a large number of long chain alkanes, phenols, aromatic hydrocarbon, which could hardly be oxidative decomposed in anaerobic fermentation [9]. The negative effect of the long chain alkanes to the anaerobic fermentation could attribute the toxicity of these alkanes to cell membranes, so as to inhibit the growth of bacteria [64–67]. And GC/MS images also proved that the remaining PAM in the solution have decomposed into acrylamide which had a BOD/COD ratio over 0.97 [68,69], hence increase the BOD value and greatly promoted the biodegradability of the wastewater, also explained that the COD value decreased greatly after the PAM treatment while BOD value had a mild change.

Comparing all three treating methods, the BOD values of each trail had a mild change comparing to the changes in COD values. This clearly demonstrated the conclusions in FTIR and GC/MS analysis, that most refractory organic pollutants aromatic hydrocarbon, alkanes, and phenols were removed within the treating process, while the contents of biodegradable substrate had smaller changes within the process.

4. Conclusions

The results and observations listed in this research indicated the importance of selecting the suitable coagulants and adsorbent, determining optimal dosage ratio, and treating sequence in the treatment of wastewater from food waste HTC. The general conclusions are extracted as following:

1) The study has identified PAFS and AC is the ideal coagulant and adsorbent in the combined coagulation and adsorption process, as the optimal treatment process is combined coagulation-adsorption, when the dosage for PAFS and AC is 6 g/L and 30 g/L, it can achieve 44.04% of the COD removal ratio, reduced COD from 41,825 mg/L to 23,825 mg/L.
2) The study demonstrated the coagulation combined AC adsorption has synergistic effect, which enhances the netting mechanism and sweeping effect by forming flocs, the adsorption efficiency was promoted, and eventually promoted the COD removal ratio of the wastewater than other individual procedures.
3) Furthermore, using PAM as coagulant of the coagulation can increase the COD removal ratio, with the addition of PAM in the dosage is 10 mg/L, it can achieve 68.41% of the COD removal ratio, indicated the sweeping and bridging effect of PAM as coagulant aid.
4) By analyzing the sediment with SEM, it was demonstrated the adsorption effect of AC micropores. Furthermore, it was indicated that xarthene, carbamide, ferulic acid and inorganic compounds composed of calcium, magnesium, and aluminum plasma were detected from the sediment of coagulation combined adsorption in XRD analysis, which proved the synergistic effect of the coagulation combined AC adsorption within this treating process.
5) FTIR and GC/MS analysis proved that the coagulation combined AC adsorption could greatly reduce the number of organic pollutants within the HTC wastewater, from 19 to 9 kinds. Additionally, within the addition of PAM as the coagulant aid, the typical organic pollutants could be reduced to 8 kinds.
6) By measuring the BOD values from each optimal group and calculating the BOD/COD ratio, by removing a large number refectory organics. It was proved that the coagulation combined adsorption method greatly promoted the potential for further biochemical treatment of the wastewater.

With the optimal process in this study, the coagulation combined adsorption could be considered as a promising method in HTC wastewater pretreatment.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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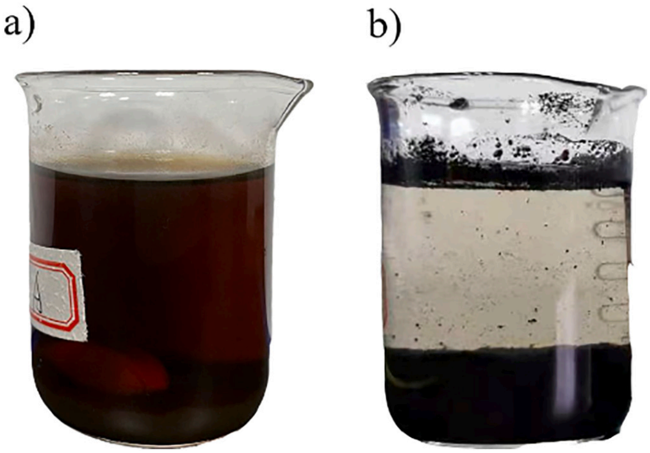
CRediT authorship contribution statement

Ruixiong Hu: writing and analysis; Yu Liu: analysis; Gaojun Zhu: analysis; Cheng Chen: analysis;

Dwi Hantoko: analysis; Mi Yan: supervision.

Appendix A



Appendices 1. Water samples (a) original wastewater; (b) waste water treated by PAM, PAFS and AC adsorption.

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