Recirculation of activated sludge for coagulant synthesis under hydrothermal conditions

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Abstract
A hypothesis was proposed that the activated sludge was converted into hydrochar full of phenolic hydroxyl and then was made into coagulant by graft copolymerization. The results show that under the addition of HCl, the content of phenolic hydroxyl on the surface of hydrochar (SBC) under hydrothermal conditions increased sharply, up to 1.586 mmol/g, showing that HCl dosage of 0.10 g/g dry sludge and holding time of 4 h was recommended. Under graft copolymerization with the addition of DMC, the coagulant was synthesized. Based on the analysis by FTIR, XPS, zeta potential, etc., the possible synthesis route of coagulant from SBC was that phenolic hydroxyl on SBC was activated by the initiator and then the polymerization between SBC and DMC was triggered. The optimal grafting conditions are gotten. It was named as SBC_{HCl0.10\;g,\;4\;h-g-DMC0.7}. The removal by SBC_{HCl0.10\;g,\;4\;h-g-DMC0.7} on COD and turbidity in domestic wastewater is up to 69% and 93%, respectively. The component of COD indicated that almost all particulate COD and most of colloidal COD are removed. On the contrary, the removal on dissolved COD can be neglected. Most of NH₃-N and P is kept in the wastewater. This is in favor of subsequent reuse and biological treatment.

Keywords Hydrochar · Hydrothermal · Graft copolymerization · Recycle · Domestic wastewater · Sludge

Introduction
The power consumption during the sewage treatment is about 1 to 3% of the total power consumption of the whole society (Zhixiao 2017), and the potential chemical energy contained in urban life sewage is up to 1.5 ~ 1.9 KW h/m³ (McCarty et al. 2011), which is nearly 5 times the energy consumption required for its treatment. If we can capture some COD chemical energy in sewage and convert it into electric energy, the sewage plant can achieve energy self-sufficient and even excess energy (Wan et al. 2016).

It is generally believed that the concentration of COD with 2000 mg/L or more is suitable for direct anaerobic energy utilization (Xiong et al. 2019). However, the concentration of organic matter in municipal domestic wastewater is low, which makes it impossible to carry out direct anaerobic methane or produce organic compound products economically and efficiently. Therefore, obtaining higher concentrations of organic matter through enrichment is a prerequisite for recovery and utilization.

There are three routes to achieve enrichment of organic matter. The first is bioflocculation and adsorption, which can obtain organic sludge with high solids content. Yet, this approach may lead to partial conversion and decomposition of some organic matter, resulting in carbon loss. The second is physical retention, i.e., the use of membrane media to separate organic matter from the wastewater, thus obtaining organic matter with higher concentration. The third is the physical flocculation and separation. This method has...
the unique advantage of low energy consumption and low loss of organic matter conversion, compared with bioflocculation. Therefore, the key is the enhanced coagulant with efficient concentration and aggregation characteristics and good solid–liquid separation performance. It is noticeable that the coagulant should be organic material for physical flocculation; otherwise, the inorganic coagulant will produce negative effect on anaerobic digestion and the quality of product due to the concentrated organic matter from wastewater. It has been reported that the addition of Al-coagulant can significantly restrain sludge hydrolysis by reducing the organic reactivity and accessibility of sludge to enzymes and bacteria due to the adsorption of organic matter by coagulant (Yaoming et al. 2018). For instance, when 24 mg–Al/L sewage was dosed into wastewater, the volatile fatty acid yield of chemically enhanced primary sedimentation sludge was about 35% lower than that of simple primary sludge (Lin-LinRuo-hongLi 2017).

Hydrothermal carbonization (HTC), also known as wet carbonization, is a thermochemical process that converts organic raw materials into high carbon solid materials at a certain temperature (160–250 °C) in a closed system in the presence of water, and the resulting solid material is called hydrochar (Libra et al. 2014; Mumme et al. 2011; Hoekman et al. 2013). Hydrochar has a core–shell structure, consisting of a hydrophobic core (containing ethers, quinones, pyrones, etc.) and a hydrophilic shell (containing a large number of oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl groups) (Fuertes et al. 2010) indicating that it has the potential to prepare carbon based aggregation media with coagulation properties by modification. It is well known that activated sludge in domestic wastewater treatment plant is full of organic matter, which is suitable to be raw materials to produce hydrochar under hydrothermal conditions.

It has been reported that the polyol structure (phenolic OH) on the surface of lignin is the most important functional group and is the reaction site to easily install dithioester as a chain transfer agent for fragmentpolymerization. Therefore, lignin can be used as a core material to facilitate the preparation of lignin-based doby star copolymer flocculants (Liu et al. 2019). (Chen et al. 2020) used the “grafting method” to synthesize highly efficient lignin-grafted cationic polyacrylamide (L-CPA) flocculants by first synthesizing a linear prepolymer of cationic polyacrylamide (CPA) terminated with chlorine and then grafting it onto lignin by reacting chlorine with the phenolic hydroxyl groups in the lignin molecule.

The abovementioned studies show that phenolic hydroxyl (-OH) and carboxylic (-COOH) are the key to modify the hydrochar into coagulant, its quality depending on the phenolic hydroxyl and carboxylic content. Bohli and Ouederni (2016) and Li et al. (2016) proved that the use of phosphoric acid in the activation process could produce a large amount of acid groups on the surface of activated carbon. Moreover, HNO₃ treatment primarily led to an increase in carboxyl and phenol, while the increase in lactone groups was minimal (Ahmed et al. 2016). Wang et al. (2020) reported that HCl-modified hydrochar from wheat straw showed a significant growth on the surface carboxyl (-COOH) and hydroxyl (-OH) groups compared to unmodified hydrochar. Meanwhile, alkali modification can also increase the functional groups on the surface of hydrochar, and NaOH modification can improve the amount of -OH and -COOH of hydrochar through oxidation (Xiaoliu et al. 2019) when Pinus sylvestris was used to make hydrochar. However, there is little information published to show the enhancement on the formation of phenolic hydroxyl and carboxyl on the surface of hydrochar when the activated sludge was used as the raw material under hydrothermal conditions.

Coagulant production can depend on graft copolymerization, which means first introducing the initiator of hydroxyl or carboxyl group to the raw material surface under milder reaction conditions (normally 20–150 °C), followed by in situ polymerization with modification to dope the desired target-activated monomer (Boyu and Kunquan 2018). It is suggested that hydrochar, which is gotten from activated sludge under hydrothermal conditions, has the potential to be modified to coagulant due to lots of phenolic hydroxyl on the surface of hydrochar.

This study is focusing on investigation of the synthesis of coagulant with the hydrochar from activated sludge under hydrothermal conditions by graft copolymerization. It is to assess the following: (1) the phenolic hydroxyl and carboxyl formation under different hydrothermal conditions; (2) the relationship between phenolic hydroxyl, carboxyl, and coagulant synthesis and its performance on aggregation organic matter in wastewater; and (3) the mechanism of the phenolic hydroxyl to make coagulant. The aim is to clarify the probability and mechanism of transferring activated sludge into coagulant by hydrothermal conditions and graft copolymerization to enrich organic matter in wastewater.

Materials and methods

Materials and reagents

Materials

Mechanically dewatered sludge (recorded as SS) from a wastewater treatment plant in Suzhou, with a water content of (84 ± 0.27)%, TSS of (70 ± 0.54)%, and pH between 7 and 8; HCl, methacryloyloxyethyl trimethyl ammonium chloride (DMC), potassium persulfate (KPS), analytical pure; Kaolin, chemically pure, Tianjin Fuchen Chemical Reagent Factory.
Reagents

Hydrothermal reactor (temperature ≤ 350 °C, pressure ≤ 10 MPa, with mechanical stirring and precise temperature control function), UV spectrophotometer (Shimadzu UVmini-1280), portable turbidity meter (Hash 2100Q), COD tester, etc.

The process of synthetic reaction

Preparation of SBC

First of all, dewatered sludge was obtained from the domestic wastewater treatment plant in Suzhou. The dewatered sludge was mixed with a certain amount of catalyst and added into the hydrothermal reaction kettle under hydrothermal conditions with the stirring speed of 200 r·min⁻¹, the hydrothermal temperature of 170 °C and the holding time of 4 h. The catalysts were set as NaOH, KOH, Na₂CO₃, CaCO₃, HCl, and HNO₃, and the catalyst concentrations were 0.04, 0.06, 0.08, 0.1, and 0.12 g/g dry sludge. After the reaction, the reaction kettle was cooled to room temperature, and the mixture was removed from the kettle for solid–liquid separation by vacuum filtration, and the separated solid product (i.e., hydrothermal carbon) was dried and ground at 105 °C and named as SBC.

Preparation of SBC-g-DMC

One gram of SBC and 50 mL of deionized water were added into a four-necked flask and then the temperature in the flask was raised to 50 °C. During the reaction, N₂ was imported into the flask for 30 min to eliminate the oxygen from the reaction system. Next, 0.1 g of KPS as the initiator was induced and kept for 10 min to pretreat the hydrothermal carbon by the initiator to inhibit the formation of PDMC (Sonmez et al. 2002). After that, 1.33 g of DMC solution (75% mass fraction) was slowly added dropwise to the solution. The temperature was adjusted to 70 °C and the reaction was kept at the constant temperature of 70 °C for 4 h to obtain a light yellow solid–liquid mixture. Eventually, the solid–liquid was separated and the solid was dried under vacuum at 75 °C to obtain a brown powder, which is the aggregation medium (coagulant).

Grafting ratio (GR) and grafting efficiency (GE)

The grafting rate refers to the amount of DMC grafted onto the hydrothermal carbon as a percentage of the total mass of the hydrothermal carbon (Jyothi et al. 2010). The magnitude of the grafting rate can indicate the amount of cationic monomers that have been introduced into the hydrothermal carbon, which suggests the strength of the positive charge carried by the polymerization product. Grafting efficiency refers to the amount of DMC grafted onto the hydrothermal carbon as a percentage of the total mass of DMC. It is calculated by the following equation:

\[
GR = \frac{W_1 - W_0}{W_0} \times 100\%
\]  

\[
GE = \frac{W_1 - W_0}{W_2} \times 100\%
\]

where \( W_0 \) is the mass of SB, g; \( W_1 \) is the mass of aggregation medium, g; and \( W_2 \) is the mass of DMC, g.

Cationic degree (CD)

The cationic degree (CD) of SBC-g-DMC was estimated by colloidal titration method, using toluidine orchid (TBO) as indicator and titrating the specimen solution with polyvinyl potassium sulfate (PVSK) standard solution (Yi et al. 2014). CD (mmol·g⁻¹) was calculated according to Eq. (3):

\[
X = \frac{C \times (V_1 - V_2)}{m \times \frac{5}{100}}
\]

where:
- Concentration of PVSK standard solution, mol·L⁻¹;
- \( V_1 \) volume of PVSK solution consumed for titration, mL;
- \( V_2 \) volume of PVSK solution consumed by titrating the blank sample, mL;
- \( m \) sample weight, g.

Sample characterizations

Scanning electron microscope images (SEM) were obtained by Hitachi S-4800 to depict surface morphologies of the products. FT-IR spectra were obtained using a UK Inter-spec 2020 spectrolab spectrometer in the range of 400 to 4000 cm⁻¹. The functional groups were determined by X-ray photoelectron spectroscopy (XPS, DMAX/2C, Shimadu). X-ray diffractometer (PANalytical X’ Pert, Spectris Pte. Ltd., Dutch) with a CuKα radiation (\( k = 1.54056 \) Å, 40 kV, 40 mA, \( 2\theta = 10–90^\circ \)) was used to investigate the crystal structures of the samples. Zeta potential (ZP) test instrument (Nano-ZS90, Malvern, England) was employed to measure the zeta potentials of different samples. The recorded values were given by nephelometric turbidity units (NTU).

Flocculation experiments

The preparation of kaolin suspension is as follows: 1 g of kaolin was put into 4 L of deionized water and then stirred well at 300 r·min⁻¹.
The flocculation processes are as following. The solution was firstly stirred at 120 r·min⁻¹ for 60 s at high speed, then stirred at 80 r·min⁻¹ for 4 min, and finally stirred at 30 r·min⁻¹ for 15 min at slow speed. After that, the solution was left to settle for 30 min, and the resulting supernatants were used for analysis.

To evaluate the removal on turbidity by SBC-g-DMC (coagulant), flocculation experiments were set. Four sets of Plexiglas tubes (i.d. 100 mm, height 160 mm) with 5 cm height of kaolin suspension was used for the experiment, called E1, E2, E3 and E4, and then each set contained 56 samples. E1 is set to evaluate the efficiency of SBC-g-DMC with different ratio of DMC to SBC from 0.4 to 1.2 on the removal of turbidity and the dosage of SBC-g-DMC is set from 1 to 8 mg/L. E2 is set to evaluate the efficiency of SBC-g-DMC with different grafting time from 1 to 5 h on the removal of turbidity and the dosage of SBC-g-DMC is set from 1 to 8 mg/L. E3 is set to evaluate the efficiency of SBC-g-DMC with different grafting pH values from 1 to 11 on the removal of turbidity and the dosage of SBC-g-DMC is set from 1 to 8 mg/L. E4 is set to ensure the efficiency of unmodified hydrochar on the removal of turbidity; dewatered sludge, SBC170, 4 g, 4 h were used in the experiments. The dosage is set from 10 to 120 mg/L.

The best SBC-g-DMC was selected according to the optimal grafting conditions and then was used to evaluate the enrichment of organic matter from domestic wastewater. The dosage is set at 10, 20, 30, 40, 50, and 60 mg/L. After the enrichment, COD and turbidity in the supernatants were analyzed.

**Results and discussion**

**Formation of phenolic hydroxyl under different catalyst**

The effect of catalyst on the acidic groups on the surface of hydrochar produced from activated sludge under hydrothermal conditions was presented in Table 1. Table 1 shows that total acidic groups varied from 0.768 to 2.792 mmol/g, depending on the catalyst. It is obvious that under HCl and HNO₃ conditions, the content of total acidic groups is higher than that under other catalyst, up to 1.718 mmol/g. It is calculated that the average percentage of phenolic hydroxyl to total acidic groups, up to 55.68%, is higher than lactone of 17.91% and carboxyl of 26.41%, respectively. It is noticed that not only the content but also the percentage of phenolic hydroxyl are the highest under the catalyst of HCl, compared with other catalysts. In addition, the sum of phenolic hydroxyl and carboxyl ranks the first. It is indicating that HCl as the catalyst is in favor of the formation of phenolic hydroxyl on the surface of hydrochar gotten from activated sludge under hydrothermal conditions. The main reason is attributed to lots of organic component hydrolysis in the activated sludge with the addition of catalyst under hydrothermal conditions, promoting the formation of phenolic hydroxyl groups. Another explanation is that the catalyst can destroy the pore walls and expand the pores, exposing more oxygen-containing functional groups (Hadjittofi et al. 2014), such as phenolic hydroxyl and carboxyl.

Additionally, the effect of HCl dosage, 0.04, 0.06, 0.08, 0.1, and 0.12 g/g dry sludge, on the acidic groups on the surface of hydrochar produced from activated sludge under hydrothermal conditions was investigated as shown in Table 2. Table 2 shows that the content of phenolic hydroxyl increased with the increase of HCl dosage, up to 1.586 mmol/g with the dosage of 0.10 g/g dry sludge, indicating that the addition of HCl was in favor of the formation of phenolic hydroxyl on the surface of hydrochar produced from activated sludge under hydrothermal conditions. It is attributed to the increase of specific surface area for the hydrochar under the addition of HCl (Jiawen et al. 2019a). It is shown that the number of oxygen-containing functional groups is highly positively related with the concentration of catalyst (Yavuz and Zeki 2014).

| Table 1 Effect of catalyst on acidic groups on the surface of hydrochar |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sample   | Acidic groups, mmol/g SBC | Phenolic hydroxyl | Lactone | Carboxyl | Total acidic groups |
|----------|---------------------------|-------------------|---------|---------|--------------------|
| SBC₁₇₀  | 0.463                     | 0.142             | 0.163   | 7.68    |
| SBCNaOH | 0.688                     | 0.106             | 0.519   | 1.313   |
| SBCKOH  | 0.528                     | 0.696             | 0.302   | 1.526   |
| SBCHCl  | 1.343                     | 0.154             | 0.375   | 1.872   |
| SBCHNO₃| 0.906                     | 0.264             | 0.803   | 1.973   |
| SBCNa₂CO₃| 0.864                     | 0.251             | 0.241   | 1.356   |
| SBCCaCO₃| 0.856                     | 0.183             | 0.362   | 1.401   |

| Table 2 Effect of catalyst concentration on acidic groups on the surface of hydrochar |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sample   | Acidic groups, mmol/g SBC | Phenolic hydroxyl | Lactone | Carboxyl | Total acidic groups |
|----------|---------------------------|-------------------|---------|---------|--------------------|
| SBCHCl₀.04 | 1.129                    | 0.121             | 0.576   | 1.826   |
| SBCHCl₀.06 | 1.343                    | 0.154             | 0.375   | 1.872   |
| SBCHCl₀.08 | 1.431                    | 0.379             | 0.798   | 2.608   |
| SBCHCl₀.10 | 1.586                    | 0.533             | 0.673   | 2.792   |
| SBCHCl₀.12 | 1.562                    | 0.354             | 0.375   | 2.291   |
However, the percentage of phenolic hydroxyl to the total acidic groups showed different trend compared with its content, decreasing with the dosage of HCl increase. It is observed that the percentage is only 56.81% at 0.10 g/g dry sludge lower than that 60.29%, without the addition of catalyst (Table 1). It is suggested that the addition of HCl not only improved the formation of phenolic hydroxyl but also enhanced the other groups, resulting in the total acidic groups increase. Total acidic groups showed the same trend as phenolic hydroxyl. On the contrary, there was no obvious relationship between the content of carboxyl and the dosage of HCl. Therefore, the further study is needed to improve the formation of phenolic hydroxyl and limit the formation of carboxyl for the hydrochar production from activated sludge under hydrothermal conditions with the addition of catalyst.

The effect of HCl holding time, 1, 2, 3, 4, and 5 h, under hydrothermal conditions on the formation of phenolic hydroxyl was presented in Table 3. According to Table 3, holding time of HCl has important effect on the formation of phenolic hydroxyl. The content of phenolic hydroxyl increased obviously with the increase of holding time, up to 1.586 mmol/g with the holding time of 4 h. It is suggesting that long holding time is better for the formation of phenolic hydroxyl. However, the hydrothermal conditions (170 °C, 4 h) are contradictory to previous study, which shows that lower temperature (150 °C) and shorter holding time (40 min) were the optimal hydrothermal conditions to form phenolic hydroxyl (Santana et al. 2022). Making comparison between two studies, the only difference was the raw material. Activated sludge was used in the study, while lignin was used in previous study. For the lignin, it is showing that ether bond which was broken improved the formation of phenolic hydroxyl, but self-polymerization of phenolic hydroxyl appeared under higher temperature and longer holding time. According to the abovementioned studies, it is speculated that the formation of phenolic hydroxyl did not come from ether bond broken because the component and structure of activated sludge were more complex than the lignin. However, the mechanism is needed to be investigated further.

According to Tables 1, 2, and 3, the optimal hydrothermal conditions for the formation of phenolic hydroxyl on the surface of hydrochar from activated sludge are as following. The catalyst is HCl and the dosage of HCl is 0.10 g/g dry sludge and the holding time is 4 h. Therefore, the SBC was named SBCHCl0.10 g, 4 h.

In many studies, the possibility of preparing hydrochar at low temperatures was explored, such as sludge-based biochar (100–180 °C) (Chuan et al. 2020), root powder–based hydrochar (100–200 °C) (Liu et al. 2021), sewage sludge and pinewood sawdust–based hydrochar (160–280 °C) (Wang et al. 2021), coconut husk–based hydrochar (140–200 °C) (Kamonwat et al. 2017), and coffee bean–based hydrochar (150–250 °C) (Mozarte et al. 2020). Typical macromolecules such as proteins and lipids still persist on the surface of the hydrochar produced at lower hydrothermal temperatures. Hence, we can assume that the solid product manufactured at low temperatures in this experiment can equally be called hydrochar.

Till now, there are little information about the formation of phenolic hydroxyl on hydrochar from activated sludge under hydrothermal conditions. Making the comparison between pyrolysis conditions and hydrothermal conditions, the results are shown in Table 4. According to Table 4, the content of phenolic hydroxyl under pyrolysis conditions with the addition of H3PO4 is 2.579 times higher than that of under hydrothermal conditions with the addition of HCl (in the study). It is indicating that H3PO4 is more suitable to enhance the formation of phenolic hydroxyl compared with HCl. However, the pyrolysis temperature is up to 500 °C, obviously higher than hydrothermal temperature of (170 °C). The application on engineering is not economical. In addition, under pyrolysis conditions, with the addition of H3PO4, the content of phenolic hydroxyl is not very high for olive stone–activated carbon and coconut shell carbon compared with this study, suggesting that the activated sludge is more suitable to produce phenolic hydroxyl. It is noticeable that under pyrolysis conditions, with the addition of KOH, the content of phenolic hydroxyl is up to 1.733 mmol/g, higher than that in the study with the addition of not only HCl (1.586 mmol/g) but also KOH (0.528 mmol/g) (Table 1).

### Synthesis of SBC-g-DMC with the hydrochar

Graft copolymerization was used to make coagulant with hydrochar from activated sludge under hydrothermal conditions. The effect of monomer (DMC) dosage, grafting time, and pH on GR, GE, and CD was investigated (Figs. 1, 2, and 3).

It is observed that GR and CD presented the increasing trend with the dosage increase, while GE presented uptrend
firstly, up to 13.16% at the dosage of DMC/SBC$_{\text{HCl0.10g,4h}}$ with 0.7:1, and then showed downtrend. It is well known that GE is referred to the amount of DMC grafted onto the hydrothermal carbon as a percentage of the total mass of DMC. It is indicating that most active points (may be phenolic hydroxyl) on the hydrothermal carbon was occupied by

| Sample                          | Catalyst Ratio (mass precursor/vol chemical agent) | Pyrolysis temperature and activation time | Functional groups (mmol/g) | References                  |
|---------------------------------|--------------------------------------------------|------------------------------------------|-----------------------------|----------------------------|
| Commercial activated carbon    | —                                                | —                                        | 0.590 0.020 0.200           | (Hunsom and Autthanit 2013) |
| Sludge-derived activated carbon| H$_3$PO$_4$ —                                    | 500 °C, 30 min                          | 4.091 1.538 3.997           | (Hunsom and Autthanit 2013) |
| Sludge-derived activated carbon| K$_2$CO$_3$ —                                    | 500 °C, 30 min                          | 1.248 0.081 2.110           | (Hunsom and Autthanit 2013) |
| Sludge-derived activated carbon| KOH —                                            | 500 °C, 30 min                          | 0.113 0 1.259               | (Hunsom and Autthanit 2013) |
| Yarn sludge activated carbon   | KI, KOH 1:0.5:0.5                                 | 700 °C, 1 h                             | 0.425 0.175 0.975           | (Tang and Zaini 2021)      |
| Olive stone–activated carbon   | H$_3$PO$_4$ 1:0.5                                 | 410 °C, 2.5 h                           | 0.835 0.405 0.512           | (Bohli and Ouederni 2016)  |
| Pet coke-activated carbon      | KOH 1:1                                          | 600 °C, 15 min                          | 1.733 0.294 1.545           | (Mochizuki et al. 2016)    |
| Coconut shell carbon           | H$_3$PO$_4$ 1:0.5                                 | 800 °C, 4 h                             | 1.390 0 1.526               | (Valencia et al. 2022)     |
| Coconut shell carbon           | ZnCl$_2$ 1:0.5                                    | 800 °C, 4 h                             | 0.027 0 0.155               | (Valencia et al. 2022)     |
| Straw-based carbon             | —                                                | 300 °C, 3 h                             | 1.230 0 1.000               | (He et al. 2022)           |
| Golden shower carbon           | K$_2$CO$_3$ 1:1                                   | 800 °C, 4 h                             | 0.190 0.340 0.250           | (Tran et al. 2017)         |
| Camellia seed husk carbon      | —                                                | 300 °C, 1 h                             | 0.450 0.270 0.160           | (Jiawen et al. 2019b)      |
| Camellia seed husk carbon      | HCl —                                             | 5 h                                     | 0.471 0.469 0.389           | (Jiawen et al. 2019b)      |
| Sludge-based hydrochar         | HCl 10:1                                         | 170 °C, 4 h                             | 1.586 0.533 0.673           | This study                 |
DMC; although the ratio of DMC/\(\text{SBCHCl}_{0.10\ \text{g},\ 4\ \text{h}}\) enhanced, the efficiency of DMC on hydrothermal carbon is decreased sharply. However, with the dosage increase, GR increased markedly. The explanation might be the electrostatic repulsion of quaternary ammonium groups on the grafted branched chains and the spatial site resistance curbed the collision between DMC and hydrothermal carbon (Leiuan 2015). Therefore, the DMC was not grafted successfully on hydrothermal carbon. Another explanation may be attributed to phenolic hydroxyl reduction. Based on Fig. 1, the preparation of \(\text{SBCHCl}_{0.10\ \text{g},\ 4\ \text{h}}\)-g-DMC is a better mass ratio of DMC to \(\text{SBCHCl}_{0.10\ \text{g},\ 4\ \text{h}}\) of 0.7:1.

With grafting time increase, GR, GE, and CD increased firstly and then showed the decrease trend (Fig. 2). It is
observed that grafting time of 3.5 h is the optimal conditions for the synthesis of SBCHCl0.10 g, 4 h-g-DMC with the hydrochar. At grafting time of 3.5 h, GR, GE, and CD is up to 10.40%, 14.86%, and 2.43 mmol/g. Nevertheless, when grafting time was greater than 3.5 h, the negative effect on GR, GE, and CD appeared because the availability of active sites on the hydrochar was reduced to make it difficult to continue the grafting between DMC and hydrochar.

According to Fig. 3, GR, GE, and CD showed the same trend as the grating time (Fig. 2) with the increase of solution pH. When the solution pH is 3, GR, GE, and CD is 10.92%, 14.90%, and 2.43 mmol/g, respectively, higher than that under other pHs. It was explained that phenolic hydroxyl group is full of high activity under acidic conditions. This was more conducive to the chain initiation reaction as free radicals, which were easily generated under the action of KPS. On the contrary, alkaline conditions have negative effect on GR, GE, and CD. It is very clear that GR, GE, and CD is 5.9%, 8.27%, and 0.45 mmol/g, respectively, under the pH of 11. This was explained that phenolic hydroxyl activity was easily ionized to phenolic oxygen negative ions under alkaline conditions, which made it difficult to generate reactive radicals under the action of initiator. Meanwhile, the hydrogen attached to the β-carbon is easily attacked by the hydroxide ions.
resulting in the instability and decomposition of the quaternary ammonium group into tertiary ammonium groups (Chunyu 2011).

According to Figs. 1, 2, and 3, for the production of coagulant (SBC<sub>HCl0.10 g. 4 h-g-DMC</sub>), the optimal grafting conditions can be described as DMC to SBC<sub>HCl0.10 g. 4 h</sub> of 0.7:1, grafting time of 3.5 h, pH of 3. The other grafting conditions are shown in “Preparation of SBC-g-DMC.” Therefore, the coagulant is named SBC<sub>HCl0.10 g. 4 h-g-DMC0.7</sub>.

However, it is noticeable that GR in the study is lower obviously (9.21%) than that in the previous study (M and A 2015), up to 21.98%. M and A (2015) reported that polydiallyldimethylammonium chloride (poly DADMAC) was used to modify cassava starch by graft copolymerization. The optimal conditions were as follows: DMDAAC to starch of 1.96, grafting time of 4.99 h. It is obvious that the amount of monomer in the previous study is 2.4 times higher than our study. The most important is that the monomer of DMDAAC has the ability to realize self-polymerization without the addition of cassava starch. It is showing that increasing the ratio of DMC to SBC<sub>HCl0.10 g. 4 h</sub> can enhance GR. Figure 1 shows that GR is increased to 13.15% when the ratio is up to 1.2, but GE is only 10%, lower markedly than that 13.16% (the ratio is 0.7). Therefore, it is suggested that GE cannot be neglected for the graft copolymerization.

**Flocculation of SBC<sub>HCl0.10 g. 4 h-g-DMC</sub> under different grafting conditions**

The efficiency of the coagulant (SBC<sub>HCl0.10 g. 4 h-g-DMC</sub>) was evaluated by flocculation on kaolin suspensions (Fig. 4). Figure 4a shows the effect of different ratio of DMC to SBC<sub>HCl0.10 g. 4 h</sub> on the turbidity removal. Figure 4b shows the effect of different grafting time on the turbidity removal. Figure 4c shows the effect of different grafting pH on the turbidity removal. The removal on turbidity by dewatered sludge without hydrothermal treatment, SBC<sub>170,4</sub> with hydrothermal treatment but without catalyst modification, and SBC<sub>HCl0.10 g. 4 h</sub> with hydrothermal treatment under the addition of HCl was compared in Fig. 4d.

Figure 4a presents that the efficiency on turbidity removal increased gradually by the SBC<sub>HCl0.10 g. 4 h-g-DMC</sub> with the increase of DMC to SBC<sub>HCl0.10 g. 4 h</sub> ratio under grafting conditions. Another, the effect of dosage of SBC<sub>HCl0.10 g. 4 h-g-DMC</sub> on turbidity removal was not marked, especially under higher ratio of DMC to SBC<sub>HCl0.10 g. 4 h</sub>. It is obvious that the efficiency on turbidity removal is highest under the DMC to SBC<sub>HCl0.10 g. 4 h</sub> ratio of 1.2, up to 96.08% (average). This is slightly higher than that under other ratios. It is in correspondence with the previous study by (M and A 2015). Making correlation analysis between GR, GE, CD, and turbidity removal under different ratio of DMC to SBC<sub>HCl0.10 g. 4 h</sub>, it is showing that GR and CD have positive obviously relationship with the ratios of DMC to SBC<sub>HCl0.10 g. 4 h</sub>. Additionally, there is a positive obvious relationship between GR, CD, and turbidity removal, $R^2$ up to 0.5576 and 0.7536, respectively. It is indicating that GR and CD are two key factors affecting the efficiency on turbidity removal by SBC<sub>HCl0.10 g. 4 h-g-DMC</sub>. According to the difference of 3% on turbidity removal between DMC to SBC<sub>HCl0.10 g. 4 h</sub> ratio of 0.7 and DMC to SBC<sub>HCl0.10 g. 4 h</sub> ratio of 1.2, DMC to SBC<sub>HCl0.10 g. 4 h</sub> ratio of 0.7 can be accepted.

Figure 4b presents the effect of different grafting time on the turbidity removal. It is puzzled that the effect of grafting time on the turbidity removal kept constant, average removal under different grafting time ranging from 92.05 to 94.71%. It is suggesting that the effect of grafting time on SBC<sub>HCl0.10 g. 4 h-g-DMC</sub> to remove turbidity can be neglected. On the contrary, the effect of grafting pH on SBC<sub>HCl0.10 g. 4 h-g-DMC</sub> to remove turbidity is obvious (Fig. 4c). Under acid conditions, the removal is higher than that under alkaline conditions. The best removal appeared at grafting pH of 3, up to 92.5% (average). It is interesting that this is in correspondence with GR, GE, and CD (Fig. 3).

Additionally, Fig. 4d shows that the dewatered sludge, SBC<sub>170,4</sub>, has no ability to remove turbidity. Compared with SBC<sub>HCl0.10 g. 4 h-g-DMC</sub>, the removal on turbidity by dewatered sludge, SBC<sub>HCl0.10 g. 4 h</sub>, can be neglected. It is verified that hydrothermal treatment and graft copolymerization are necessary to transform activated sludge into coagulant.
Both attributed to the introduction of C-spectroscopy (Fig. 6). It could be seen from Fig. 6 that graft copolymerization was characterized using infrared FTIR analysis.

The structure of the hydrothermal carbon before and after DMC monomer medium (Chauhan et al. 2015). DMC fundamentally disrupts the crystallinity of the aggregation medium after the introduction of DMC monomer (Zhen et al. 2019a). The methyl group may be related to the weakened intramolecular and intermolecular interactions between -OH groups, which fundamentally disrupts the crystallinity of the aggregation medium (Chauhan et al. 2015).

**Morphology**

Surface morphology of hydrothermal carbon before and after graft copolymerization was observed using scanning electron microscopy, and the results are shown in Fig. 5.

Figure 5a shows that the surface of SBC was blocky and irregular in shape. After graft copolymerization, the surface of SBC_{HCl0.10 g, 4 h-g-DMC0.7} (Fig. 5b) was concave and convex, full of more cracks and pores compared with SBC_{HCl0.10 g, 4 h} (Fig. 5a), resulting in its higher specific surface area than that of SBC_{HCl0.10 g, 4 h}. It is suggesting that the huge specific surface area can increase the adsorption bridging effect of the aggregation medium by increasing the contact opportunities between pollutants and copolymers (Li et al. 2017). The transformation of the surface morphology of the carbon-based aggregation medium after the introduction of DMC monomer may be related to the weakened intramolecular and intermolecular interactions between -OH groups, which fundamentally disrupts the crystallinity of the aggregation medium (Chauhan et al. 2015).

**FTIR analysis**

The structure of the hydrothermal carbon before and after graft copolymerization was characterized using infrared spectroscopy (Fig. 6). It could be seen from Fig. 6 that both SBC_{HCl0.10 g, 4 h} and SBC_{HCl0.10 g, 4 h-g-DMC0.7} have adsorption peak at 3400 cm\(^{-1}\), which may be due to the stretching vibration of O–H. In addition, the peak intensity of the stretching vibration peak of SBC_{HCl0.10 g, 4 h-g-DMC0.7} was weakened at this point. The main reason is that some of the phenolic hydroxyl groups have been successfully grafted to DMC (Zhen et al. 2019a). The methyl C-H stretching compound is near 2930 cm\(^{-1}\) and the methylene C-H stretching compound is near 2860 cm\(^{-1}\) for the SBC_{HCl0.10 g, 4 h-g-DMC0.7} spectrum. The stretching vibration absorption peak of C=O at 1727 cm\(^{-1}\) was attributed to the introduction of C=O in the DMC structure, and the new absorption peak at 1481 cm\(^{-1}\) was a stretching vibration absorption peak of -CH\(_2\)-N\(^+\)(CH\(_3\))\(_3\) in the quaternary ammonium group (Li 2014). Therefore, graft copolymerization between hydrothermal carbon and monomeric DMC can be verified by this.

**XPS analysis**

The XPS fully scanned spectra of SBC_{HCl0.10 g, 4 h} and SBC_{HCl0.10 g, 4 h-g-DMC0.7} are shown in Fig. 7a. It could be seen from Fig. 7a that the major elements of both samples were C, N, and O, but the elemental ratios were different completely. Additionally, the increase of N element ratio on SBC_{HCl0.10 g, 4 h-g-DMC0.7} compared with SBC\(_4\) proved the successful grafting of DMC monomer on hydrothermal carbon.

The XPS spectra of C 1 s for SBC_{HCl0.10 g, 4 h} and SBC_{HCl0.10 g, 4 h-g-DMC0.7} are shown in Fig. 7b and c, respectively. The C 1 s spectrum of MCC contains three peaks. The peak at 284.4 eV is associated with C–C/H bonds in the hydrochar, especially the methyl and methylene groups on the surface of the hydrochar. A total of 286.3 eV peak was usually attributed to C-O bonds in the hydroxyl (C–OH) and ether (C–O–C) groups, or due to the formation of polycyclic nitrogenous compounds. And 288 eV peak could be attributed to carbonyl C-O and O-C-O bonds in the carboxyl groups on the surface of the hydrochar. After modification, the peaks of these groups moved from 284.4 eV, 285.3 eV, and 288 eV to 284.3 eV, 285.4 eV, and 287.8 eV, correspondingly. In addition, the intensity of the C–C peak was improved and that of the C-O/C-N and O-C-O peaks decreased. These are the verification for the grafting of DMC on hydrothermal carbon.

For the O 1 s spectra in Fig. 7d and e, the peak of 531.7 eV could be attributed to C-O/C–OH. After modification by DMC, the C-O/C–OH bond was slightly deflected. However, the modification of C-O/C–OH peak area was negligible. It was mainly attributed to the double effect of polymerization process. On the one hand, the grafting process consumed the amount of C–OH on the surface of hydrothermal carbon. On the other hand, the transport of C-O from DMC (Zhen et al. 2019b) to SBC_{HCl0.10 g, 4 h-g-DMC0.7} was enhanced during the grafting process.

Figure 7f and g show the N 1 s spectra of SBC_{HCl0.10 g, 4 h} and SBC_{HCl0.10 g, 4 h-g-DMC0.7}. It is shown that the peak appearing at 401.5 eV belonged to -(CH\(_2\))\(_2\)-N\(^+\)(CH\(_3\))\(_2\), while 399.7 eV corresponded to the NH\(_2\)CO\(^-\) structure. Compared with SBC_{HCl0.10 g, 4 h}, the intensity of both peaks was higher for SBC_{HCl0.10 g, 4 h-g-DMC0.7}. It is furtherly confirmed the success of DMC grafting (Laurent et al. 2001).

**XRD analysis**

The XRD maps of SBC_{HCl0.10 g, 4 h} and SBC_{HCl0.10 g, 4 h-g-DMC0.7} were shown in Fig. 8. The diffraction peak of...
SBCHCl0.10 g, 4 h-g-DMC0.7 was obviously weaker compared with SBCHCl0.10 g, 4 h. It is indicating that the crystalline region of hydrothermal carbon was damaged to some extent and the crystallinity was reduced.

Zeta potential

The charge characteristics of coagulant have a great influence on its flocculation effect. Therefore, we measured the pH dependence of different materials zeta potential, as shown in Fig. 9. Zeta potential for SBCHCl0.10 g, 4 h-g-DMC0.7 in the pH range of 3.0–11.0 stayed at the higher level than that for SBCHCl0.10 g, 4 h. In addition, SBCHCl0.10 g, 4 h-g-DMC0.7 exhibits a clear cationic polyelectrolyte characteristic in the pH range of 3.0–11.0 due to the grafting of strong cationic quaternary ammonium salt groups. It is interesting that zeta potential under acidic conditions is higher than that under alkaline conditions. One explanation is that the ionization of quaternary ammonium salts was strongly promoted by a large amount of hydrogen ions. The other reason is that the amide group (NH₃⁺) was converted to NH₃⁺ by protonation. Therefore, pH increase resulted in the hydrolysis of quaternary ammonium salts and deprotonation of NH₃⁺. This enhanced the decrease of positive charge continuously (Wu et al. 2022).

Flocculation effect of SBCHCl0.10 g, 4 h-g-DMC0.7 on domestic wastewater

SBCHCl0.10 g, 4 h-g-DMC0.7 shows the better ability to remove COD and turbidity in domestic wastewater (Fig. 10). With the dosage of SBCHCl0.10 g, 4 h-g-DMC0.7 increase, the removal on COD and turbidity increased gradually and then kept constant. When the dosage of SBCHCl0.10 g, 4 h-g-DMC0.7 was 50 mg/L, the equilibrium concentration of COD and turbidity appeared. The mean is 69.24% and 93.09% for COD and turbidity, respectively.

In order to compare the capabilities of SBCHCl0.10 g, 4 h-g-DMC0.7 with other coagulants in the literature, we selected the relevant contributions from the following literature and present them in Table 5. SBCHCl0.10 g, 4 h-g-DMC0.7 has a relatively less dosage and relatively higher removal on COD and turbidity compared to other natural polymer flocculants. However, there is a pity that the flocculation processes, such as rotational speed, temperature, and pH, for different coagulants are not listed in detail. Therefore, it is difficult to decide the effect of flocculation process on removal on COD and turbidity. According to Table 5, it is showing that SBCHCl0.10 g, 4 h-g-DMC0.7 is an optimal selection to enrich organic matter from domestic wastewater.

Although SBCHCl0.10 g, 4 h-g-DMC0.7 has better ability to remove organic matter, not all kinds of organic matter can be removed (Fig. 10b). Figure 10b presents that the removal on particulate COD (pCOD) is the best, higher obviously than that on colloidal COD (cCOD) and dissolved COD (sCOD). In the domestic wastewater, the proportions of pCOD (granular state, > 20 μm), cCOD (colloidal and super colloidal state, 0.22–20 μm), and sCOD (dissolved state, < 0.22 μm) were 50.6%, 30.3%, and 19.1%, respectively. It is indicating that most of pCOD is removed by SBCHCl0.10 g, 4 h-g-DMC0.7, ranging from 79.65 to 94.25%. It is attributed to the cationic quaternary ammonium group possessed by SBCHCl0.10 g, 4 h-g-DMC0.7, which could produce charge neutralization with negatively charged colloidal particles in wastewater and form large flocs to settle in contact with
It is observed that the contributions of cCOD is ranking second, lower than pCOD. The removal by SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} ranged from 26.88 to 75.78%. At the dosage of SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} with 60 mg/L, the removal on cCOD is up to 75.78%. However, the removal by SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} on sCOD can be neglected. The content of sCOD kept constant when the dosage ranged from 10 to 60 mg/L. This is in favor of the subsequent biological treatment.

In addition, the removal on NH\textsubscript{3}-N and P by SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} was analyzed in the study (Fig. 11). It is shown in Fig. 11 that the removal on NH\textsubscript{3}-N by SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} can be neglected. With the addition of SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} under different dosages, the percentage of NH\textsubscript{3}-N was kept constant, 59% (mean), similar as the percentage of 64% in the domestic wastewater without the addition of SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}}. On the contrary, for other species of N, the percentage decreased from 36% (domestic wastewater) to 7% (60 mg/L dosage), indicating that SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} has better ability to remove other species of N. This is similar as other species of P in Fig. 11b. The value decreased from 37% (domestic wastewater) to 13% (60 mg/L dosage). The better removal is attributed to the better coagulation on particulate forms of N and P. In addition, the good removal of particulate organic matter (69%, average) and suspended solid (93%, average), resulting in parts of N and P removal, was another explanation. Although PO\textsubscript{4}\textsuperscript{3-}-P percentage in domestic wastewater can be decreased from 63% (domestic wastewater) to 43% (60 mg/L dosage); most of P was retained in domestic wastewater, in favor of subsequent reuse on P.

In a word, under the action of SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}} in domestic wastewater, almost all particulate organic matter (80–94%) and most colloidal organic matter (27–76%) can be enriched, and all dissolved organic matter, most of N (66–80%) and P (56–76%), were kept in domestic wastewater. It is indicating that there is no obvious effect on subsequent biological treatment and reuse on P. It has been mentioned that anaerobic ammonia oxidation denitrification and biofilm sequencing batch reactors for phosphorus recovery can be used for subsequent treatment (Yang et al. 2022).

**Synthesis mechanism of SBC\textsubscript{HClO\textsubscript{10}, 4 h-DMC\textsubscript{0.7}}**

According to the structures of SBC, DMC, and characterization analysis, the possible synthesis route was speculated as the following (Fig. 12). The synthesis
between SBC and DMC is attributed to free radical reaction. Persulfate dissociates into SO4•− free radicals, which then react with water to form •OH free radicals. Subsequently, •OH free radicals attack SBC, resulting in the formation of macromolecular radicals on SBC. Afterwards, the macromolecular radicals can react with monomers to form hydrochar-based monomer radicals. The activated monomer then reacts with another monomer and propagates the chain reaction to prepare a coagulant (SBC-g-DMC) (Maji and Maiti 2021).

Application of SBC_{HCl0.10 g, 4 h-g-DMC0.7} to enrich organic matter in domestic wastewater

More and more scientists pay attention to recycle organic matter in wastewater treatment plant. Based on our study in
the paper, recycling organic matter by main stream technology can be realized in wastewater treatment plant (Fig. 13).

The activated sludge can be converted into hydrochar, which is full of phenolic hydroxyl, under hydrothermal conditions with the addition of HCl as the catalyst, and then the coagulant can be synthesized by hydrochar and DMC under graft copolymerization.

In the main stream, the coagulant, which the dosage depends on the organic matter content in the influence, was added into the coagulation tank under mixing conditions and then the effluent went to sedimentation tank. The organic matter will be aggregated by coagulation and settled to the bottom. Finally, we could get the precipitates, which are full of organic matter. Part of these precipitates can be used to produce hydrochar under hydrothermal conditions and then the hydrochar can be grafted into coagulant by graft copolymerization in the wastewater treatment plant. The other part can be used for direct anaerobic energy utilization. It is very clear that depending on hydrothermal treatment and graft copolymerization, the circulation of organic matter in wastewater treatment plant can be a reality.

Conclusions

Under hydrothermal conditions, with the addition of HCl, it was observed that the content of phenolic hydroxy on the surface of hydrochar (SBC), coming from activated sludge, was higher obviously that other catalysts, indicating that HCl improved the formation of phenolic hydroxy. HCl dosage of 0.10 g/g dry sludge and holding time of 4 h were recommended because of the highest content of phenolic hydroxyl. Using the SBC to make coagulant under graft copolymerization was realized in the study and then the coagulant was characterized by FTIR, XPS, zeta potential, etc. According to GR, GE, CD, and flocculation results on turbidity, the optimal grafting conditions are as following. The dosage of DMC/SBC is 0.7:1 and the grafting time is 3.5 h and grafting pH is 3. Therefore, the coagulant is named as SBCHCl0.10 g, 4 h, g, DMC0.7. When it was used in domestic wastewater to enrich organic matter, it is observed that COD removal is 69% (average) under different dosages. In addition, the removal of the particulate COD is up to 94%, while colloidal COD removal is only 76%. On the contrary, there is no removal on dissolved COD, which is beneficial of subsequent biological treatment. Additionally, most of NH3-N and P were retained in wastewater, in favor of subsequent reuse.

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Data availability All data and materials have been provided within the manuscript.

Declarations

Ethics approval and consent to participate Not applicable.

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References

Ahmed MB, Zhou JL, Ngo HH, Guo W, Chen M (2016) Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresour Technol 214:836–851

Assaad S, Najwa M, Nadhem S, Rafik B, Ali B (2014) Chitin and chitosan extracted from shrimp waste using fish proteases aided process: efficiency of chitosan in the treatment of unhauling effluents. J Polym Environ 22(1)

Bohli T, Ouederni A (2016) Improvement of oxygen-containing functional groups on olive stones activated carbon by ozone and nitric acid for heavy metals removal from aqueous phase. Environ Sci Pollut Res 23(16):15852–15861

Boyu L, Kunquan L (2018) Effect of nitric acid pre-oxidation concentration on pore structure and nitrogen/oxygen active decoration sites of ethylenediamine-modified biochar for mercury(II) adsorption and the possible mechanism. Chemosphere 220.

Chauhan K, Priya V, Singh P, Chauhan GS, Kumari S, Singhal RK (2015) A green and highly efficient sulfur functionalization of starch. RSC Advances 5(64)

Chen N, Liu W, Huang J, Qiu X (2020) Preparation of octopus-like lignin-grafted cationic polyacrylamide flocculant and its application for water flocculation. Int J Biol Macromol 146:99–105

Chuan C, Guangmin L, Qing A, Lin L, Yong S, Chunli W (2020) From wasted sludge to valuable biochar by low temperature hydrothermal carbonization treatment: insight into the surface characteristics. J Clean Prod 263(C)

Chunyu W (2011) Preparation and characterization of graft copolymers from enzymatic hydrolysis lignin and glycine. Polym Mater Sci Eng 27 No. 11, 168–170+175

Fuertes AB, Arbeestain MC, Sevilla M, Macía-Agulló JA, Fiol S, López R, Smernik RJ, Aitkenhead WP, Arce F, Macías F (2010) Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. Soil Res 48(7):618

Guo LX (2017) Experimental study on chitosan-polyferric chloride flocculant for the treatment of urban sewage. Ind Water Treat

Hadjittofi L, Prodromou M, Pashalidis I (2014) Activated biochar derived from cactus fibres – preparation, characterization and application on Cu(II) removal from aqueous solutions. Bioresour Technol 159460–464.
Hameed YT, Idris A, Hussain SA, Abdullah N (2016) A tannin-based agent for coagulation and flocculation of municipal wastewater: chemical composition, performance assessment compared to Polyaluminum chloride, and application in a pilot plant. J Environ Manag 184:494–503.

He X, Hong Z, Shi R, Cui J, Lai H, Lu H, Xu R (2022) The effects of H2O2- and HNO3/H2SO4-modified biochars on the resistance of acid paddy soil to acidification. Environ Pollut 293:118588.

Hoekman SK, Broch A, Robbins C, Zielinska B, Felix L (2013) Hydrothermal carbonization (HTC) of selected woody and herbaceous biomass feedstocks. Biomass Convers Biorefinery 3(2):113–126

Hunsom M, Autfahan C (2013) Adsorptive purification of crude glycerol by sewage sludge-derived activated carbon prepared by chemical activation with H3PO4, K2CO3 and KOH. Chem Eng J 229:334–343.

Jiawen W, Tao W, Yongsheng Z, Wei-Ping P (2019a) The distribution of Pb(II)/Cd(II) adsorption mechanisms on biochars from aqueous solution: considering the increased oxygen functional groups by HCl treatment. Bioresour Technol 291(C).

Jiawen W, Tao W, Yongsheng Z, Wei-Ping P (2019b) The distribution of Pb(II)/Cd(II) adsorption mechanisms on biochars from aqueous solution: considering the increased oxygen functional groups by HCl treatment. Bioresour Technol 291(C).

Jyothi AN, Sajeev MS, Moorthy SN, Sreekumar J (2010) Effect of graft-copolymerization with poly(acrylamide) on rheological and thermal properties of cassava starch. J Appl Polym Sci 116(4):337–346.

Kamnawat N, Bunyarat P, Vorapot K, Nawin V, Wasawat K, Prasert P (2017) Hydrothermal carbonization of unwanted biomass material: effect of process temperature and retention time on hydrochar and liquid fraction. J Energy Inst 91(5).

Laurent D, Claude G, Sotira Y, Eric G (2001) Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy. Colloids Surf A: Physicochem Eng Asp 177(2–3).

Leian H (2015) The preparation and performance evaluation of AM-DMC-SSS-starch. Appl Chem Ind 44(01):53–56

Li T (2014) “Research on the preparation of poly-methacrylamidoethyltrimethyl ammonium chloride (PDMC).” Fine Chem 31(11):1324-1328+1375

Li K, Jiang Y, Wang X, Bai D, Li H, Zheng Z (2016) Effect of nitric acid modification on the lead(II) adsorption of mesoporous biochars with different mesopore size distributions. Clean Technol Environ Policy 18(3):797–805

Li X, Zheng H, Gao B, Zhao C, Sun Y (2017) UV-initiated polymerization of acid- and alkali-resistant cationic flocculant P(A-MAPTAC): synthesis, characterization, and application in sludge dewatering. Sep Purif Technol 187:244–254.

Libra JA, Ro KS, Kammann C, Funke A, Berge ND, Neubauer Y, Titirici M, Fühner C, Bens O, Kern J, Emmerich K (2014) Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels 2(1):71–106

Lilinruo-Hongli (2017) Effect of coagulant on acidigenic fermentation of sludge from enhanced primary sedimentation for resource recovery: Comparison between FeCl3 and PACI1.

Liu Z, Lu X, Xie J, Feng B, Han Q (2019) Synthesis of a novel tunable lignin-based star copolymer and its flocculation performance in the treatment of kaolin suspension. Sep Purif Technol 210:355–363.

Liu L, Sim SF, Lin S, Wan J, Zhang W, Li Q, Peng C (2021) Integrated structural and chemical analyses for HCl-supported hydrochar and their adsorption mechanisms for aqueous sulfachloropyridazine removal. J Hazard Mater 417.

M AAR, A A (2015) Polymeric flocculant based on cassava starch grafted polydiallyldimethylammonium chloride: flocculation behavior and mechanism. Appl Surf Sci 351.

Maji B, Maiti S (2021) Chemical modification of xanthan gum through graft copolymerization: tailored properties and potential applications in drug delivery and wastewater treatment. Carbohydr Polym 251:117095.

McCarty PL, Bae J, Kim J (2011) Domestic wastewater treatment as a net energy producer – can this be achieved? Environ Sci Technol 45(17):7100–7106

Mochizuki T, Kabota M, Matsuda H, D’elio Camacho LF (2016) Adsorption behaviors of ammonia and hydrogen sulfide on activated carbon prepared from petroleum coke by KOH chemical activation. Fuel Process Technol 144:164–169

Mozarte SS, Rafael PA, Willian MDSB, Elton F, Mário CG (2020) Hydrochar production from defective coffee beans by hydrothermal carbonization. Bioresour Technol 300(C).

Mumme J, Eckervogt L, Pielet J, Diaikté M, Rupp F, Kern J (2011) Hydrothermal carbonization of anaerobically digested maize silage. Biores Technol 102(19):9255–9260

Patil SV, Patil CD, Salunke BK, Salunke RB, Bathe GA, Patil DM (2011) Studies on characterization of biofloculants expolyolsaccharide of Azotobacter indicus and its potential for wastewater treatment. Appl Biochem Biotechnol 163(4).

Sajjad H, Javed AA (2008) Characterization and treatability studies of tannery wastewater using chemically enhanced primary treatment (CEPT) – a case study of Saddiq Leather Works. J Hazard Mater 163(2).

Santana MS, Alves RP, Santana LS, Goncalves MA, Guerreiro MC (2022) Structural, inorganic, and adsorptive properties of hydrochars obtained by hydrothermal carbonization of coffee waste. J Environ Manag 302:114021.

Sonmez HB, Senkal BF, Bicak N (2002) “Poly(acrylamide) grafts on spherical bead polymers for extremely selective removal of mercuric ions from aqueous solutions”. Journal of polymer science. Part A Polymer Chem 40(17):3068–3078

Tang SH, Zaini MAA (2021) Microporous activated carbon prepared from yarn processing sludge via composite chemical activation for excellent adsorptive removal of malachite green. Surf Interfaces 22.

Tran HN, You S, Chao H (2017) Fast and efficient adsorption of methylene green 5 on activated carbon prepared from new chemical activation method. J Environ Manag 188:322–336

Valencia A, Muñiz-Valencia R, Ceballos-Magaña SG, Rojas-Mayorga CK, Bonilla-Petriciolet A, González J, Aguayo-Villarreal IA (2022) Cyclohexane and benzene separation by fixed-bed adsorption on activated carbons prepared from coconut shell. Environ Technol Innov 25:102076

Wan J, Gu J, Zhao Q, Liu Y (2016) COD capture: a feasible option towards energy self-sufficient domestic wastewater treatment. Scientific Reports 6(1).

Wang S, Ai S, Nzediegwu C, Kwak J, Islam MS, Li Y, Chang SX (2020) Carboxyl and hydroxyl groups enhance ammonium adsorption capacity of iron (III) chloride and hydrochloric acid modified biochars. Bioresour Technol 309:123390.

Wang R, Lin K, Ren D, Peng P, Zhao Z, Yin Q, Gao P (2021) Energy conversion performance in co-hydrothermal carbonization of sewage sludge and pinewood sawdust coupling with anaerobic digestion of the produced wastewater. Sci Total Environ 803.

Wu Y, Jiang J, Sun Q, An Y, Zhao R, Zheng H, Li H (2022) Efficient removal of both positively and negatively charged colloidal contaminants using amphoteric starch-based flocculants synthesized by low-pressure UV initiation. Sep Purif Technol 282:120120.
Xiaoliu W, Yingying L, Lingjun Z, Yunchao L, Kaige W, Kunzan Q, Nakorn T, Pruk A, Prasert R, Shurong W (2019) Biomass derived N-doped biochar as efficient catalyst supports for CO2 methanation. J CO2 Utilization 34(C)

Xiong J, Yu S, Hu Y, Yang Y, Wang XC (2019) Applying a dynamic membrane filtration (DMF) process for domestic wastewater pre-concentration: organics recovery and bioenergy production potential analysis. Sci Total Environ 680:35–43

Yang W, Shan J, Pan Y, Bi Z, Huang Y, Zhang H, Ni M (2022) A new strategy for obtaining highly concentrated phosphorus recovery solution in biofilm phosphorus recovery process. J Environ Sci 112:366–375

Yaoming C, Yanxin W, Dongbo W, Hailong L, Qilin W, Yiwen L, Lai P, Qi Y, Xiaoming L, Guangming Z, Yanrong C (2018) Understanding the mechanisms of how poly aluminium chloride inhibits short-chain fatty acids production from anaerobic fermentation of waste activated sludge. Chem Eng J 334

Yavuz G, Zeki A (2014) Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. Appl Surf Sci 313

Yi L, Huaili Z, Li Q, Yongjien S, Li D, Wenwen X (2014) UV-initiated polymerization of hydrophobically associating cationic polyacrylamide modified by a surface-active monomer: a comparative study of synthesis, characterization, and sludge dewatering performance. Ind Eng Chem Res 53(27)

Zafar A, Schj Dt-Thomsen J, Sodhi R, Goacher R, De Kubber D (2012) X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry characterization of aging effects on the mineral fibers treated with aminopropylislane and quaternary ammonium compounds. Surf Interface Anal: SIA: an Int J Devoted Dev Appl Tech Anal Surf Interfaces Thin Films 44(7):811–818

Zhen W, Wenxiu H, Guihua Y, Yu L, Sai L (2019a) Preparation of cellulose-base amphoteric flocculant and its application in the treatment of wastewater. Carbohydr Polym 215

Zhen W, Wenxiu H, Guihua Y, Yu L, Sai L (2019b) Preparation of cellulose-base amphoteric flocculant and its application in the treatment of wastewater. Carbohydr Polym 215.

Zhen W, Wenxiu H, Guihua Y, Yu L, Sai L (2019c) Preparation of cellulose-base amphoteric flocculant and its application in the treatment of wastewater. Carbohydr Polym 215.

Zhixiao L (2017) Carbon capture and carbon redirection: new way to optimize the energy self-sufficient of wastewater treatment. China Water Wastewater 33(08):43–52

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