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Effect of Fenton pre-oxidation on the physicochemical properties of Sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal

--Manuscript Draft--

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Abstract:	Fenton pre-oxidation, as a promising technology for sludge deep dehydration, has been used intensively; however, the outputs (i.e., low-water-content sludge cakes) need to be further disposed for a full line sludge resource utilization. Carbonization presents a promising approach for disposing of the sludge cake within the process. Here, the physicochemical properties of sludge-based char obtained after Fenton pre-oxidation were studied. Both Fenton pre-oxidized sludge-based char (FSC) and raw sludge-based char (RSC) were produced within the temperature range of 400 ℃ to 600 ℃, and the adsorption performance of the prepared chars, exemplified by their ability to adsorb ammonia nitrogen (NH4+), was tested under various conditions. FSC exhibited superior char yield and adsorption performance compared to RSC, with chemical adsorption being the primary controlling factor. The optimum conditions for FSC were observed at 400 ℃, resulting in a char yield of 72.2%, and an adsorption capacity of 221.7 mg/g. Notably, FSC demonstrated an increase in C-C, C-N, O=C-O, C-O and C=C functional groups in comparison to RSC, which suggests that pre-oxidation increases organic matter decomposition and chemical reactivity of the sludge. The introduction of Si-O-Si, Si-O-C and Fe-O-H functional groups in the FSC facilitated ion exchange with NH4+ in an aqueous solution. The key findings indicate that Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for excellent-char preparation. These results demonstrated the potential to integrate sludge deep dewatering, including pre-oxidation, with char preparation.

Response to reviewers

Effect of Fenton pre-oxidation on the physicochemical properties of Sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal
(Ref. JECE-D-23-04956)

Dear Editor Prof. Apostolos Giannis,

The authors gratefully acknowledge the valuable comments made by the reviewers. We have studied their comments carefully and have made correction which we hope meet with their approval. The changes in the revised manuscript are highlighted in blue according to the referee's comments.

Reviewer 1:

Issue 1:
In my opinion it is an interesting investigation and in general terms it is well done, but there are certain aspects that may be subject to discussion.
Page 15, end of section 3.1.2. From "Therefore, in order to analyze..." to "...fixed at 60 minutes." has already been explained above. This paragraph can be deleted.

Response 1:
Thank you for the pointing out the omission. According to the comment of the reviewer, we have deleted this part as following,
"Above all, the carbonization temperature plays a more important role in char formation and yield than residence time, since a residence time of 60 min is sufficient to achieve optimal char yield while minimizing energy consumption." (Line 254 to 256)

Issue 2:
- The kinetic study I think has not been carried out properly. It is surprising that adsorption occurs by one mechanism and at the same time by a different mechanism. The case of an intermediate mechanism in which the value of R2 would be far from 1 for both models is not proposed. The authors propose that both kinetic mechanisms are true, which is incongruent.
There is an explanation for this fact and it is a mistake that the authors have probably (as I can see from Fig 6B) made. There is one set of data that fits both models in any adsorption phenomenon studied: those where equilibrium has been reached. And most of the data presented in figure 6B are such data. But the study of kinetic models is interesting because it tells us how we get to equilibrium, not what happens at equilibrium. Theoretical models have to be applied to experimental data prior to equilibrium. I think you should repeat the experiment with shorter times.
- Continuing with this theme, in figures 6B and 6C there is hardly any difference

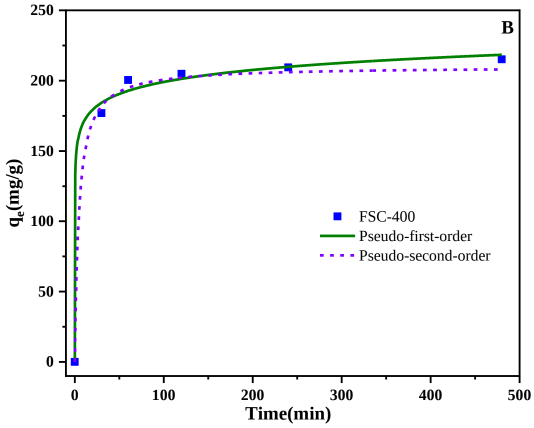
between the lines of the two models proposed in each figure. Although we live in a world that tends more and more towards visual communication, I believe that sometimes information is clearer if it is presented in the form of numerical tables. I therefore suggest that tables S2 and S3 be included in the main text.

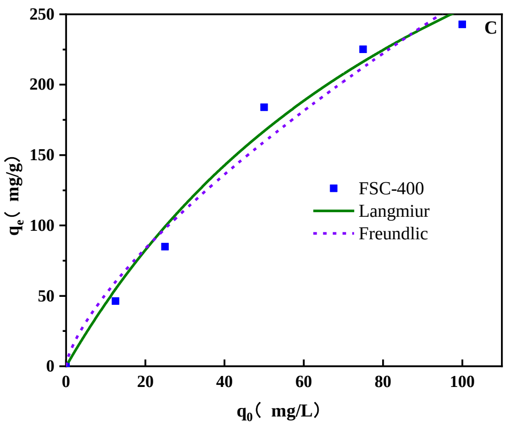
Response 2:

Thank you for your comment. Regarding issue 2 and 3, both of which are related to the kinetic study, we answered the questions together. We have carefully reviewed the reviewer's comments and made the necessary revisions to address the concerns raised. After thorough consideration and consulting relevant books and literatures, we acknowledge that the kinetics equations are generally derived under specific conditions within the equilibrium zone. According to the reviewer's suggestion, we conducted additional experiments with shorter times, and based on the obtained data, we have redrawn Figure 6B and 6C, and incorporated Table 4 and 5 in the main text. The results were more clearly presented. (Line 397 to 423)

“The results of the dynamics model’s equations and adsorption isotherms of FSC are presented in Fig. 6 B and 6C, as well as Table 4 and 5. The kinetic analysis of ammonia nitrogen adsorption on FSC indicates that it followed pseudo-second-order, as evidenced by the high values of R^2 (greater than 0.9964) in Fig. 6B.”

“The Langmuir model provided a better fit to the experimental data compared to the Freundlich model, as shown in Table 5, indicating that the adsorption process follows homogeneous monolayer adsorption.”





B. Ammonia nitrogen isotherms on FSC-400 and dynamics fitting models; C. Ammonia nitrogen isotherms on FSC-400 and adsorption fitting models

Table 4 Parameters of adsorption dynamic model

Model	K	q_e	R^2
pseude-first-order	1.23±0.674	204.95±6.72	0.9688
pseude-second-order	0.001±1.745	209.44±5.00	0.9964

Table 5 Parameters of adsorption isotherm model

Model	K	Q/n	R^2
Langmuir	0.0082±8.7E-5	56.35±0.39	0.9959
Freundlich	10.09±4.54	1.42±0.21	0.9885

We believe that these modifications significantly improve the accuracy and presentation of the kinetic study, thereby strengthening the overall quality of the manuscript.

Issue 3:

- Page 28, lines 444 to 447. The authors propose that the carbon dioxide that can be generated is primarily responsible for changes in porosity. I believe this statement should be revised for the following reasons:

a) Activation with carbon dioxide is usually carried out at higher temperatures than those used in this research, as it is a molecule with limited reactivity.

b) During carbonization, it is possible that part of the solid structure may be destroyed by temperature. This includes pore walls and usually results in a wider porosity.

c) N_2 adsorption at low pressures is higher in the RSC series, so presumably the treatment decreases the number and volume of micropores contrary to the authors' claims.

Response 3:

We thank the reviewer for raising valuable points regarding the proposed role of carbon dioxide in the changes in porosity. Upon careful consideration and consulting relevant literature, we acknowledge that carbon dioxide is more likely to be generated at a slight level at 400 ^oC, as the activation with carbon dioxide typically occurs at higher temperatures due to its limited reactivity. Based on the suggestion from the reviewer, we have provided the following explanation: The Fenton pre-oxidation process led to the degradation of the biopolymers and the conversion of sludge flocs into small fragments [26]. This transformation has significant benefits for pore development during carbonization, as it enhanced decarboxylation reactions and caused partial destruction of the solid structure, resulting in a wider porosity. Additionally, Fenton oxidation promoted the transition from micropores to mesopores (Fig.5). (Line 453 to 459)

By considering these factors, we agree that the role of carbon dioxide in the observed changes in porosity should be revised, and we appreciate the reviewer's valuable insights that have helped improve the accuracy and clarity of our explanation.

Reviewer 2:

Issue 1:

The novelty or specific contribution to knowledge should be clearly emphasized in abstract as well as the text.

Accordingly, the authors should expand further on the literature review. If this is not the first time this technology has been used, what exactly have the authors done differently?

Response 1:

According to the suggestion of reviewer, we have revised the Abstract and the relevant part in the text to emphasize the novelty and specific contribution of our study.

In the Abstract, we now clearly state that our study demonstrates the novelty contribution of using Fenton pre-oxidation as a component for the carbonization process. “The key findings indicate that Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for excellent-char preparation. These results demonstrated the potential to integrate sludge deep dewatering, including pre-oxidation, with char preparation.” (Line 39 to 43)

Furthermore, as per the reviewer's comment, we have enhanced the literature review section (Introduction) by incorporating relevant references to previous studies: Lin et al. and Li et al. found that Fenton conditioning greatly enhanced the adsorption capacity by affecting the porosity of the sludge [26, 27]. Belete et al. reported that the Fenton reagents increased the acidic group's concentration and the BET surface area, but without changing the morphology [28]. However, our study contributes to the existing body of knowledge by exploring the relatively limited discussions on the impact of Fenton pre-oxidation on the physicochemical properties of char surfaces and its subsequent effects on the adsorption mechanism. (Line 88 to 95)

We also have enhanced the conclusion section: These findings highlight the effectiveness of Fenton pre-oxidation on sludge-based char, and present it as a promising technology by integrating the dehydration and carbonization process with lower energy consumption. (Line 511 to 514)

Issue 2:

How were the optimum conditions stated in the abstract and elsewhere in the body arrived at? One could not find any specific objective and/or the mathematical model used for this? Or, on what basis?

Response 2:

Thank you for your inquiry. The determination of the optimum conditions, specifically the carbonization temperature of 400℃, was based on the following considerations:

1. Highest adsorption capacity: Experimental results indicated that the adsorption capacity of the Fenton sludge-based biochar (FSC) was the highest at a carbonization temperature of 400℃, reaching 221.7 mg/g. This value was compared to higher temperatures, where the adsorption capacity was lower. The significant increase in adsorption capacity at 400℃ can be attributed to the enhanced performance of FSC due to Fenton pre-oxidation.
2. Char yield optimization: Additionally, the char yield achieved at 400℃ was the highest at 72.2%. This means that a substantial amount of biochar is obtained at this temperature, which translates to lower energy consumption and higher returns. The higher char yield at 400℃ further supports the selection of this temperature as the optimum condition.
3. Integration of dehydration and carbonization: Another essential aspect considered is the integration of the dehydration and carbonization process. Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for the preparation of excellent-char. This integration results in lower overall energy consumption, making the technology more promising and efficient.

These points collectively supported the selection of 400℃ as the optimum carbonization temperature. It ensured the highest adsorption capacity, optimal char yield, and energy-efficient integration of the dehydration and carbonization processes. We believe that these factors contribute to the significance and validity of the chosen conditions.

Issue 3:

Was the FS prepared in this research?

Response 3:

Yes, in this research, the FS was indeed prepared. We followed the specific preparation procedures and used the optimal condition that was obtained in our previous study. We have revised the section 2.1 Materials and provided additional information:

"The RS was obtained from the secondary sedimentation tank, with a moisture content of 82.5%. The FS was prepared following the procedures and the optimum conditions obtained in our previous study [7]. The mole ratio H_2O_2: Fe^{2+} was 2. The content of catalyst $FeSO_4 \cdot 7H_2O$ was 6% (m/m), and the concentration of oxidants H_2O_2 was 30%. Under these specified conditions, the moisture content of FS was successfully reduced to 53.2%." (Line 127 to 133)

Issue 4:

Line 26/27: "pseude-first-order (3) and pseude-second-order r (4) model" What are these "pseude" orders? Did the authors mean "pseudo"?

Response 4:

We apologize for the oversight. Based on the reviewer's comment, we have revised the word "pseude" to "pseudo". We appreciate the reviewer's feedback and attention to detail. (Line 199)

Reviewer 3:

Issue 1:

I have reviewed the paper entitled 'Effect of Fenton pre-oxidation on the physicochemical properties of Sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal'. The paper presents relevant information. It is well designed and easy to follow. The applied methodology is adequate, and the literature cited is actualized. It deserves publication in Journal of Environmental Chemical Engineering after Major Revisions. The authors must consider the following comments:

- What is the significance of this study? The novelty of this work should be further highlighted. The authors should clarify the principal motivation behind this manuscript.

Response 1:

Thank you for the valuable comments, and thank you for recognizing the innovation and originality of this article. According to your suggestion, we have made the necessary revisions to further highlight the significance and novelty of this study.

In the Abstract, we now clearly state that our study demonstrates the novelty contribution of using Fenton pre-oxidation as a component for the carbonization process. "The key findings indicate that Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for excellent-char preparation. These results demonstrated the potential to integrate sludge deep dewatering, including pre-oxidation, with char preparation.” (Line 39 to 43)

Furthermore, as per the reviewer's comment, we have enhanced the literature review section (Introduction) by incorporating relevant references to previous studies: Lin et al. and Li et al. found that Fenton conditioning greatly enhanced the adsorption capacity by affecting the porosity of the sludge [26, 27]. Belete et al. reported that the Fenton reagents increased the acidic group's concentration and the BET surface area, but without changing the morphology [28]. However, our study contributes to the existing body of knowledge by exploring the relatively limited discussions on the impact of Fenton pre-oxidation on the physicochemical properties of char surfaces and its subsequent effects on the adsorption mechanism. (Line 88 to 95)

We also have enhanced the conclusion section: These findings highlight the effectiveness of Fenton pre-oxidation on sludge-based char, and present it as a promising technology by integrating the dehydration and carbonization process with lower energy consumption. (Line 511 to 514)

Issue 2:

For keywords, please revise Line 46 and include more innovative keywords.

Response 2:

As per the reviewer's comment, we have revised the keywords that with more innovative words.

“Fenton pre-oxidation; sludge-based char; ammonia nitrogen adsorption; Surface composite modification; Structural enhancement” (Line 45 to 46)

Issue 3:

For Line 160, why the author used the word 'quality' in this sentence. Better to be removed and replaced only by 'mass'.

Response 3:

Thank you for pointing out the omission. According to the comment of the reviewer, we have revised the word “quality” to “mass”. (Line 166 to 167)

Issue 4:

Avoid repeating same words many times through the manuscript. Define the abbreviation once then just use the abbreviations.

Response 4:

Based on the reviewer's comment, we have made the necessary revision to avoid words repeated many times and only use the abbreviations after defined. We appreciate the reviewer's attention to detail and their valuable feedback.

Issue 5:

For supplementary materials, the title page with authors and affiliations should be included.

Response 5:

Thank you for pointing out the omission. According to the comment of the reviewer, we have revised the title page, and now the authors and affiliations are included in the supplementary materials.

Issue 6:

The authors should appropriately insert related references especially at the methods section. Please revise accordingly.

Response 6:

As per the reviewer's comment, we have added the necessary references to the manuscript (Section 2.4)

“For the adsorption kinetic study, a NH_4^+ solution with 50 mg/L initial concentration was applied. The behavior of the adsorption with the function of time was fitted using the pseudo-first-order (3) and pseudo-second-order (4) model [28],”

“The data were fitted to Langmuir and Freundlich model [29], the equations were as follows” (Line 199 to 200, Line 206)

Issue 7:

A cost-estimation analysis should be included in this manuscript to show the potential application of this work.

Response 7:

Thank you for the suggestion. We agree that a comprehensive economic analysis is essential to demonstrate the potential application and feasibility of the proposed technology. In our previous work, we have studied the promotion of Fenton pre-oxidation on secondary advanced dewatering of sludge on pilot scale. And we have a cost-estimation analysis of the pilot test. The total cost considered reagent cost and electricity bill primarily, resulting in a range of 98.5-113.7 CNY/t·wb [1]. In this work, we intended to prove that Fenton pre-oxidation is not only a promising technology for sludge deep dehydration, but also can synchronously improve the structure and surface properties of sludge-base char without additional consumption of materials and energy on lab scale. The results showed that pre-oxidation not only reduces the energy consumption associated with deep dehydration, but also lowers the energy requirement of carbonization, thereby significantly reducing overall energy consumption. However, we acknowledge that a complete economic analysis has not been conducted in this particular study since we primarily worked on a fixed bed at the laboratory scale. To address this, we appreciate your suggestion and plan to conduct experiments on a pilot scale to thoroughly analyze the cost estimation of integrating the dehydration and carbonization processes. By doing so, we can provide a more comprehensive understanding of the economic feasibility and practical application of this technology in larger-scale scenarios We sincerely thank you for your insightful feedback, and we are committed to enhancing the overall quality and impact of our manuscript.

[1] N. Lin, W. Zhu, X. Fan, C. Wang, C. Chen, H. Zhang, L. Chen, S. Wu, Y. Cui, Key Factor On Improving Secondary Advanced Dewatering Performance of Municipal Dewatered Sludge: Selective Oxidative Decomposition of Polysaccharides, Chemosphere, 249 (2020) 126108. https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.126108

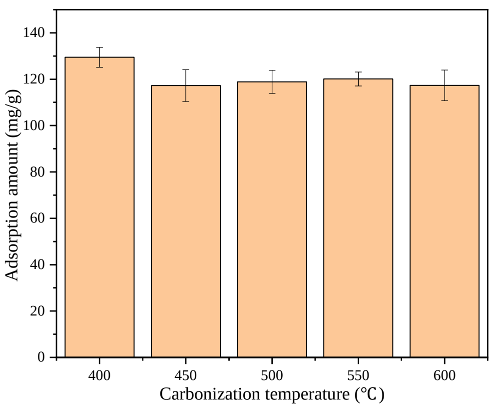
Issue 8:

Some statistics are needed for this work such as including a principal component analysis considering the impact of the different parameters on the potential ammonia adsorption using chars. This would validate the obtained results.

Response 8:

Thank you for your suggestion regarding the inclusion of a principal component analysis to validate the obtained results. We agree that statistical analysis, such as principal component analysis, can provide valuable insights into the impact of different parameters on the potential ammonia adsorption using chars. In this study, we have indeed conducted some experiments on the potential ammonia with different parameters, such as different carbonization temperatures and pH of aqueous solutions. The results were shown is the following figures. The main focus of this paper is on the effect of Fenton pre-oxidation on the performance of sludge-based biochar, so the data are mostly presented around this point. To address this, we appreciate your feedback and will ensure that the principal component analysis and further statistical analysis are included in our future work. By conducting a more in-depth analysis, we aim to reveal the complex improving mechanism proposed in this paper and gain a better understanding of the relationship between process parameters and char adsorption capacity.

We thank you for your valuable input, which has contributed to the refinement of our research approach. Your feedback is highly appreciated, and we look forward to incorporating the principal component analysis and conducting more comprehensive studies in the future



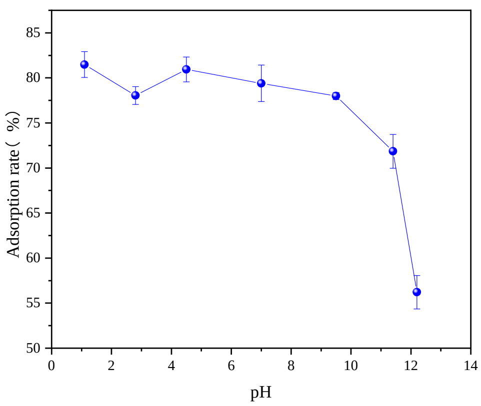


Fig.1 Effect of carbonization temperature on adsorption characteristics Fig. 2 The effect of pH on adsorption characteristic

Highlights:

1. Fenton pre-oxidation reduced the required carbonization temperature for FSC
2. Pre-oxidation modified the structure of FSC leading to greater adsorption capacity
3. The best adsorption capacity (221.7 mg/g) of FSC was achieved at 400℃
4. The study provides the possibility of integrating dehydration and carbonization

CRediT authorship contribution statement

Jun Cao: Conceptualization, Investigation, Data curation, original draft. **Ruochen Wang:** Investigation, Data curation. **Hualun Zhu:** Review & Editing. **Songshan Cao:** Methodology, Review & Editing. **Zhipeng Duan:** Review & Editing.

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Effect of Fenton pre-oxidation on the physicochemical properties of Sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal

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Abstract:

Fenton pre-oxidation, as a promising technology for sludge deep dehydration, has been used intensively; however, the outputs (i.e., low-water-content sludge cakes) need to be further disposed for a full line sludge resource utilization. Carbonization presents a promising approach for disposing of the sludge cake within the process. Here, the physicochemical properties of sludge-based char obtained after Fenton pre-oxidation were studied. Both Fenton pre-oxidized sludge-based char (FSC) and raw sludge-based char (RSC) were produced within the temperature range of 400 ℃ to 600 ℃, and the adsorption performance of the prepared chars, exemplified by their ability to adsorb ammonia nitrogen (NH_4^+), was tested under various conditions. FSC exhibited superior char yield and adsorption performance compared to RSC, with chemical adsorption being the primary controlling factor. The optimum conditions for FSC were observed at 400 ℃, resulting in a char yield of 72.2%, and an adsorption capacity of 221.7 mg/g. Notably, FSC demonstrated an increase in C-C, C-N, O=C-O, C-O and C=C functional groups in comparison to RSC, which suggests that pre-oxidation increases organic matter decomposition and chemical reactivity of the sludge. The introduction of Si-O-Si, Si-O-C and Fe-O-H functional groups in the FSC facilitated ion exchange with NH_4^+ in an aqueous solution. The key findings

indicate that Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for excellent-char preparation. These results demonstrated the potential to integrate sludge deep dewatering, including pre-oxidation, with char preparation.

Keywords*:* Fenton pre-oxidation; sludge-based char; ammonia nitrogen adsorption；Surface composite modification; Structural enhancement

1 Introduction

The challenge of achieving comprehensive treatment of sludge is becoming increasingly prevalent worldwide. With the growing collection and treatment of domestic sewage in China, the country's sewage treatment capacity has significantly increased [1]. Consequently, the disposal of sewage sludge has also experienced a rapid rise, reaching approximately 60 million tons in 2020 (80% water content). There is an urgent need to develop a technology that allows for sludge recycling while minimizing its volume and associated environmental impact. However, the high moisture content of sludge, which can reach up to 99.5wt% [2], currently poses a major obstacle disposal method due to considerable energy consumption and operational costs associated with the sequent thermal conversion technologies required for further treatment of sludge. The Fenton or

Fenton-like pre-oxidation method is widely recognized as a crucial step in the pretreatment process for achieving deep water removal [3]. This method is performed prior to subsequent thermal disposal and disintegration [4, 5]. In our previous study, we modified this technology and reduced the water content from 82.5% to 53.2% under optimal conditions (mole ratio H_2O_2: Fe^{2+} =2) [6,8]. This modification effectively reduced the volume and elevated the low calorific value of the sludge. However, it resulted in the production of a significant amount of Fe-rich sludge cake, which presents challenges for proper disposal [9]. The obtained sludge cake typically retains a significant amount of organic matter, making it a key research focus to develop sustainable treatment methods in line with the goals of “emission peak” and “carbon neutralization”.

Sludge carbonization is widely regarded as a promising method to accomplish this objective [10,12]. Carbonization can greatly reduce the weight and volume by decomposing and evaporating water, while simultaneously facilitating energy conservation and the acquisition of byproducts. Sludge-based char, due to its large specific surface area, well-developed microstructure, and abundant oxygen functional groups and aromatic compounds on the surface, exhibits characteristics of both an energy material and an adsorbent. Currently, the char finds significant applications in various fields, including fuel energy, environmental protection, materials and agriculture [3, 13,16]. An important utilization of char involves its ability to adsorb and immobilize heavy metal ions [17], as well as nitrogen, phosphorus and organics in water purification, hereby acting as a cost-effective alternative to commercial adsorbents [18]. The potential for widespread application and expansion of the means depends on whether the char prepared from pre-oxidized sludge has a high utilization value. Studies have demonstrated that the Fenton and Fenton-like char synthesized by carbonization exhibits superior performance compared to that of RS, making them efficient adsorbents for pollutant removal [19]. Until now, studies have investigated the effects of temperature, residence time, preparation materials and additives on the structural characteristics of chars [20,25]. Lin et al. and Li et al. found that Fenton conditioning greatly enhanced the adsorption capacity by affecting the porosity of the sludge [26, 27]. Belete et al. reported that the Fenton reagents increased the acidic group's concentration and the BET surface area, but without changing the morphology [28]. However, our study contributes to the existing body of knowledge by exploring the relatively limited discussions on the impact of Fenton pre-oxidation on the physicochemical properties of char surfaces and its subsequent effects on the adsorption mechanism.

In aquatic environment, excessive emission of ammonia nitrogen is a significant contributor to eutrophication, posing a threat to water resources worldwide [29]. This issue has garnered global attention and has become a hot topic of concern. Consequently, the discharge standards of ammonia nitrogen have become increasingly stringent both domestically and internationally, and the efficient removal of ammonia nitrogen from water has become a crucial objective in safeguarding aquatic environment. The biochar derived from rice straw, wheat straw, coconut shell, and other materials has been identified as a simple and low-cost adsorbent for ammonia nitrogen removal from water [30]. This is due to its large specific surface area, strong ion exchange ability, and the presence of a negative charge on the surface. Previous studies have shown that there are more oxygenated functional groups formed, and the newly Fe (III) and Fe (II) groups introduced on the Fenton and Fenton-like char. These groups may enhance the ion exchange and provide an increased number of negative charges during the adsorption process [9, 19]. Considering these findings, the removal of ammonia nitrogen using Fenton pre-oxidized sludge-based char has been identified as a potential application direction due to the favorable characteristics of the char for this purpose.

Above all, in order to evaluate the mechanism of pre-oxidation on the adsorption properties of sludge-based char, both Fenton pre-oxidized sludge (FS) and the raw sludge (RS) were used to produce chars under different carbonization temperatures and residence times. The influences of Fenton pre-oxidation on char yield, element composition, specific surface area, microstructure, and functional groups were analyzed. Furthermore, the adsorption performance of ammonia nitrogen on the char and the corresponding adsorption mechanism were also studied.

2 Materials and methods

2.1 Materials

Municipal Sludge samples were collected from Xushe Wastewater Treatment Plant located in Yixing city, China. The plant has a sewage treatment capacity of 10,000 tons per day. The plant employs the A^2O+filter processing system for municipal wastewater treatment. The RS was obtained from the secondary sedimentation tank, with a moisture content of 82.5%. The FS was prepared following the procedures and the optimum conditions obtained in our previous study [7]. The mole ratio H_2O_2: Fe^{2+} was 2. The content of catalyst $FeSO_4 \cdot 7H_2O$ was 6% (m/m), and the concentration of oxidants H_2O_2 was 30%. Under these specified conditions, the moisture content of FS was successfully reduced to 53.2%. The higher heating values (HHVs) of sludge rose with the addition of oxidants, increased from 0.06 to 7.97 MJ/kg. $FeSO_4 \cdot 7H_2O$ and H_2O_2 (30%) were both purchased from Sinopharm Chemical Reagent Co., Ltd. The samples were then crushed and screened without pre-drying before all experiments. The basic property parameters of sample RS and FS were listed in Table 1.

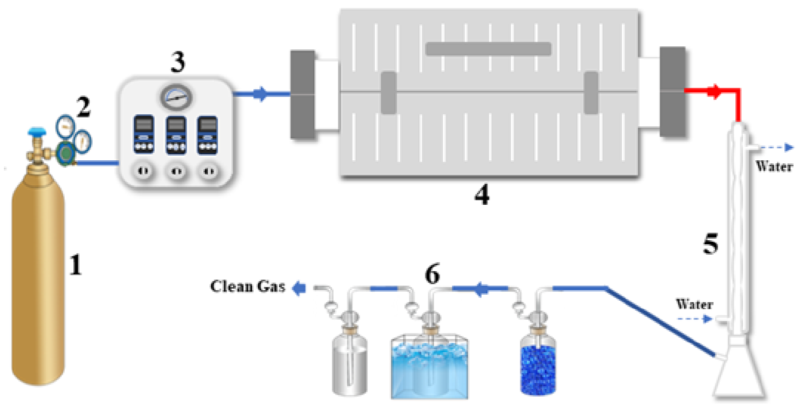
Table 1 Basic property parameters of sludge

Sample	Proximate Analysis (wt%, daf)			Elemental Analysis (%)					pH	Q_{ar}
	A_{ar}	V_{ar}	FC_{ar}	C	H	O	N	S	-	$MJ \cdot kg^{-1}$
RS	45.81	50.27	6.92	25.35	4.89	16.99	2.86	0.99	6.78	0.06
FS	42.34	51.35	3.31	23.56	4.39	18.44	3.45	1.84	4.95	7.97

2.2 Materials preparation

The sludge-based char was prepared using a system illustrated in Fig.1. An N_2 flow, which controlled by a mass flow controller, was used to maintain an inert atmosphere. The fixed bed furnace employed a quartz tube with a length of 800 mm and an inside diameter of 40 mm, heated externally by a resistance furnace controlled by a temperature programmed controller. One thermocouple was placed inside the tube to monitor the real-time temperature of the reaction zone, while the other thermocouple was set outside the tube to monitor the temperature of the reactor. The gas produced during the experiment was purified by passing it through a contented condensing device and a tail gas treatment system.

The preparation of the char proceeded as follows: First, the sludge was placed in the middle of the tube. To remove all oxygen out of the tube, N_2 was pumped-in with a flow rate of 200 ml/min for 30 min after leak checking. Then the reactor was heated at a rate of 10 °C/min, starting from room temperature to the target temperatures (400, 450, 500, 550 and 600 °C) and maintained for a certain time (30, 60, 90 and 120 min). The reactor was turned off and allowed to cool down until the furnace temperature dropped below 150 °C. Subsequently, the samples were removed from the reactor, weighted and collected. The resulting products were denoted as RSC-T and FSC-T, where T represents the target temperature. The sludge-based char yield was calculated according to the Formula 1:



1.N_2 gas cylinder; 2. Pressure reduce regulator; 3. Mass flowmeter and controller; 4. Fixed bed with electric furnace; 5. Condensing device; 6. Tail gas treatment

Fig. 1 Sludge char preparation experimental schematic diagram

$$\eta = \frac{m_0 - m_1}{m_0} \times 100\% \qquad (1)$$

where η is char yield, %; m_0 is original sludge mass, g; m_1 is mass of obtained sludge-based char, g.

2.3 Characterization and Analysis

An element analyzer (EA, EURO EA3000, Italy) was applied to determine the contents of C, H, O, N and S in sludge and char obtained at different temperatures. An acidimeter (pH, NY/T 1377.2007, China) was used to analyze the pH level and conductivity of the samples. Fourier infrared analysis (FTIR, Model Vextor 22, Germany) was conducted from 4000 to 400 cm^{-1} and each spectrum was a spectral average of at least four scans. X-ray photoelectron microscopy (XPS, Thermo Scientific ESCALAB250Xi, USA) analysis was performed and the binding energy was corrected by contaminated char (C1s, 284.6eV). The CasaXPS program was used to fit and divide peaks. The N_2 isotherm adsorption profile was obtained using an automated gas sorption analyzer (ASAP2020, Micomeritics, USA) at 77K. The specific surface areas (S_{BET}) of samples were calculated according to the Brunauer, Emmett, Teller method (BET) from the adsorption isotherms. The pore size (P_A) distribution of samples before and after calcination was calculated from desorption branch using the Barrett, Joyner and Halenda (BJH) method. Scanning electron microscope (SEM, S4800, Japan) was used to analyze the surface morphology of chars.

2.4 Ammonia nitrogen adsorption

The adsorption experiments were conducted using a set of 50 mL centrifuge tube containing 0.1 g of sludge char and 50 mL of NH_4^+ with an initial concentration of 50 mg/L in an aqueous solution. The tubes were placed on a shaker at 20 ℃ and 120 r/min. The samples were then filtered and the residual concentration of NH_4^+ was analyzed using 420 nm of Nessler reagent spectrophotometry. The adsorption capacity of NH_4^+ was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m_1} \quad (2)$$

Where, q_e represents the adsorption amount per unit mass of sludge char at adsorption equilibrium, mg/g. C_0 and C_e represent the initial and equilibrium concentrations of NH_4^+ in solution respectively, mg/L. V represents the volume of solution, mL.

For the adsorption kinetic study, a NH_4^+ solution with 50 mg/L initial concentration was applied. The behavior of the adsorption with the function of time was fitted using the pseudo-first-order (3) and pseudo-second-order (4) model [31], as followed:

$$q_t = q_e(1 - e^{-K_1 t}) \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where, t represents reaction time, min. q_t represents the sorption capacity at t time, mg/g. K_1 and K_2 represent rate constants of the two models, respectively, g/(mg·min).

The data were fitted to Langmuir and Freundlich model [32], the equations were as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

Linearized and obtained,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Linearized and obtained,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Where q_m represents saturated adsorption capacity, mg/g. K_L represents Langmuir adsorption constant. K_F represents the Langmuir adsorption constant. c_e represents the equilibrium mass concentration of ammonia nitrogen, mg/L. n represents the empirical constant.

3 Results and discussion

3.1 Carbonization

3.1.1 Effect of carbonization temperature

Fig. 2A showed the char production rate of RS and FS when the carbonization temperature rose from 400 to 600 ℃, the sample mass was 5 g and the residence time was 60 min. It can be observed that the char yield of FSC was higher than that of RSC at each temperature point, with the char production rate of FSC ranging from 62.4% to 72.2%, while that of RSC was 36.67% to 43.8%. Both FS and RS achieved the maximum char yield at 400 ℃, which were 72.2% and 43.8% respectively. With the increase of carbonization temperature, the yield of both FSC and RSC decreased. However, as the temperature further increased up to 500℃, the downward trend of sludge char yield became smaller and eventually stabilized at 550 ℃. This can be attributed to the decomposition of volatile components in the sludge, which is mostly completed by 500 ℃. At this point, further increase in temperature has a lesser effect on the char yield as the remaining components are more stable. The difference in char yield between FS and RS can be attributed to their disparate moisture content [33]. The RS had a moisture content of 82.5%, while the FS had a reduced moisture content of 53.2%. The lower moisture content in FS might lead to higher char yield, as moisture is vaporized during the carbonization process, resulting in a greater mass loss in RS compared to FS.

3.1.2 Effect of residence time

In the study conducted at 400 ℃, the effect of residence time on energy consumption and char yield was investigated. The experiments were performed with a sample weight of 5 g and residence times of 30, 60, 90, and 120 min. Fig. 2B shows that as the residence time extended from 30 min to 120 min, the decrease in char yield was 2% for FS and 1.4% for RS, respectively. This indicates that the decomposition of organic matter in the sludge had essentially completed within a residence time of 60 min. Further extending the residence time did not significantly affect the char yield, suggesting that the carbonization process had reached a relatively stable state in terms of char formation.

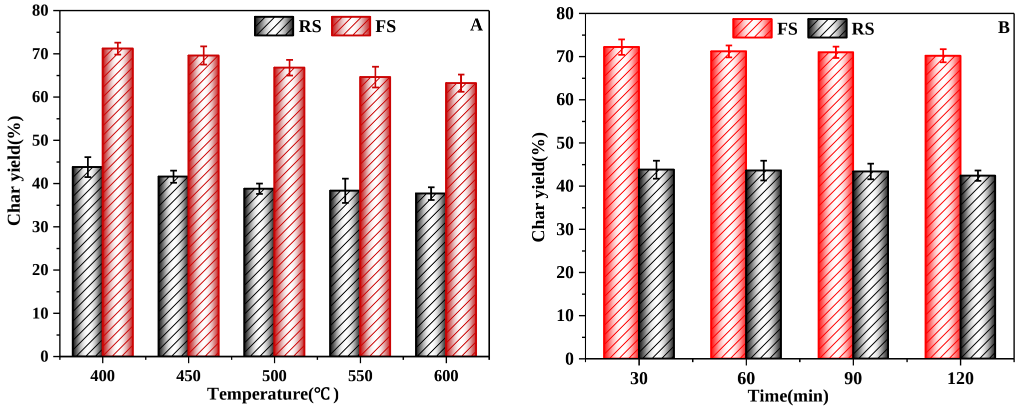


Fig. 2 A. Effect of carbonization temperature on char yield: The mass of sample was 5 g, the residence time was 60 min, the temperature was 400, 450, 500, 550, 600℃; B. Effect of residence time on char yield: The mass of sample was 5g, the temperature was 400℃ and the residence time was 30, 60, 90 and 120 min.

Above all, the carbonization temperature plays a more important role in char formation and yield than residence time, since a residence time of 60 min is sufficient to achieve optimal char yield while minimizing energy consumption.

3.2 Effect of Fenton pre-oxidation

3.2.1 Effect of Fenton pre-oxidation on elemental composition

The element composition and ash content of the char derived from different carbonization temperatures, ranging from normal atmospheric temperature to various carbonization temperatures, were carried out. The results were shown in Table 1 and Table 2. According to Table 1, the contents of ash, volatiles and S of cakes pretreated with Fenton agent were higher compared to the RS, which can be attributed to the addition of inorganic oxidants. In Table 2, it can be observed that the carbonization temperature increased, the contents of C, H, O and N, as well as the ratios of H/C, decreased for both FSC and RSC. This reduction indicated that the organic matter in the sludge was more thoroughly decomposed and released in the form of H_2O, CO_2, CO, CH_4, H_2 and NO_x with increasing temperature [4]. Thus, the content of carboxyl, hydroxyl, protein and other functional groups on the surface of char progressively decreased, indicating an increased degree of carbonization. As an important parameter to characterize the carbonization level, the decrease of H/C ratio further confirmed the enhancement of the aromaticity and stability of the char. The S content in the char showed slight growth regardless of the temperature, due to the addition of oxidants [34]. The increase of S in the char can be attributed to the addition of $FeSO_4 \cdot 7H_2O$, which exceeded the decomposition of S during the process. The O/C ratio was boosted from 0.93 for RSC-400 to 1.33 for FSC-400, and the changes of the O/C ratio could correlate with the changes of chemical functional groups including oxygen, which suggested that a surface oxidation reaction occurred during Fenton pre-oxidation, and there could be a low content of carboxylic groups on the sample surfaces [35].

Table 2 Elemental analysis and calorific value of sludge-based char

Carbonization Temperature/ ℃	Elemental analysis/%							Ash/%
T	C	H	O	N	S	H/C	O/C	-
RSC-400	17.10	1.93	15.90	2.53	0.67	0.11	0.93	61.87
RSC-450	13.15	1.37	14.17	2.01	0.97	0.10	1.08	68.33
RSC-500	12.46	1.05	12.08	1.93	0.93	0.08	0.97	71.55
RSC-550	11.31	0.85	11.43	1.66	0.84	0.08	1.01	73.91
RSC-600	11.42	0.63	10.46	1.49	0.73	0.06	0.92	75.27
FSC-400	13.41	1.70	17.90	2.24	1.53	0.13	1.33	63.12
FSC-450	12.37	1.52	17.57	2.03	1.58	0.12	1.42	64.83
FSC-500	12.14	1.31	16.26	1.84	1.65	0.11	1.34	66.7
FSC-550	11.67	1.13	15.08	1.71	1.67	0.10	1.29	68.56
FSC-600	11.72	0.97	14.24	1.59	1.55	0.08	1.22	69.44

3.2.2 Effect of Fenton pre-oxidation on surface functional groups of char

The FTIR spectra of RSC-T and FSC-T were provided in Fig. 3. An adsorption peak observed between 2300~2420 cm^{-1} may be attributed to the S-H and C-N stretching vibrations [36]. The adsorption peak around 2305~2320 cm^{-1} are due to the -COO antisymmetric stretching vibration in carboxyl group or the stretching vibration of C=O in lactone group [37]. For RS, the peak intensity was the strongest at 400 ℃. With the temperature increasing, the peak gradually disappeared, but reappeared when the temperature reached 600 ℃. The peak observed in FSC was weak when the temperature rose from 400 to 450 ℃.

However, the peak became more prominent at 500 ℃, before weakening and disappearing at 600 ℃. This suggested that the oxidation process caused a rearrangement of the functional groups in the sludge, resulting in changes in the observed peak intensity. The observed trend is consistent with the changes in the N ratio in both types of sludge. The region near 1550-1600 cm^{-1}, which only occurred in FSC-T, corresponded to the stretching vibrations of carbonyl structures of C=O and alkene of C=C bonds. This indicates that the pretreated sludge facilitates the generation of the small molecule organics and indirectly increasing C=O and C=C [38, 39]. It can be found that the surface of the sludge-based char contains various substances or functional groups such as hydroxyl, phenolic hydroxyl, carboxyl, amino, imino, lactone, anhydride, ether, ester and other substances or functional groups [40], revealing that the surface of FSC was enriched with oxygen-containing functional groups, particularly acids and aldehydes, after the pre-oxidation. The stretching vibration adsorption peaks at 1040 cm^{-1} and 976 ~ 1038 cm^{-1} can be endorsed to Si-O-Si or Si-O-C and Fe-O-H, respectively. The peaks observed in FSC-T were evidently higher than those of RSC-T, which showed that the addition of reagent ($FeSO_4 \cdot 7H_2O$) introduced new minerals. The adsorption peaks observed at 619 cm^{-1} corresponded to Si-O-Fe bonds [28, 41]. The stretching vibration adsorption peaks at 680-580 cm^{-1} corresponded to S=O and O=S=O, which are characteristic of SO_4^{2-}. The presence of these peaks suggests that sulfuric acid groups were introduced onto the surface of char [42, 43], which is consistent with the increase in S element content as shown in Table 2.

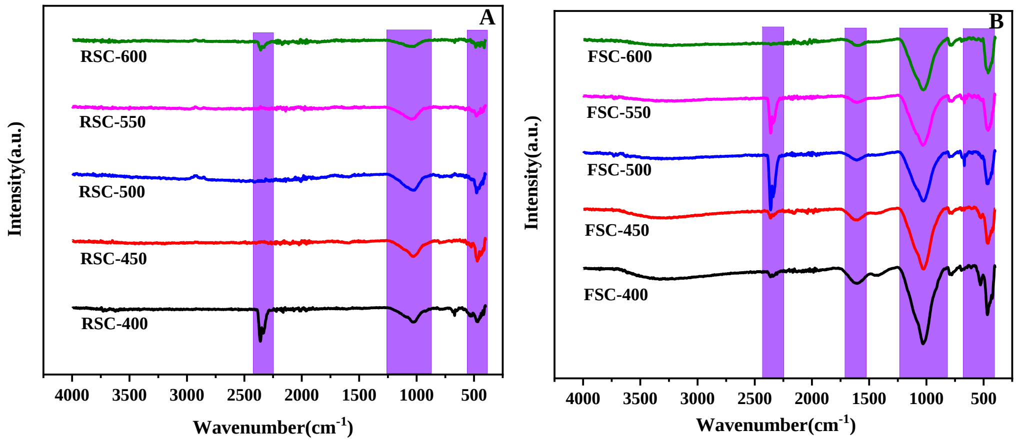


Fig. 3 A. FTIR spectra of RSC-400, RSC-450, RSC-500, RSC-550 and RSC-600; B. FTIR spectra of FSC-400, FSC-450, FSC-500, FSC-550 and FSC-600.

The effect of Fenton pre-oxidation on the carbon-containing groups on the surface of char obtained at 400 °C was investigated using XPS, as depicted in Fig. 4. The proportions of surface element content were analyzed and are presented in Table S1. The C1s peak of RSC-400 and FSC-400 was broken down into six peaks by Casa XPS software, representing typical sp^2 C=C (284.2 eV), sp^3 C-C\C-H (284.6 eV), C-O (285.4-286.0 eV), C-N (protein-N, 285.4eV) and O=C-O (288.2-290.2e) [44] as shown in Fig. 4. There was no similar variation pattern in the C content of the surface of RSC-T and FSC-T (Table S1). However, the C content on the surface of FSC-400 decreased compared to that of RSC-400. This might be due to the increase of O content resulting from the addition of the oxygen-containing reagent [45], this observation is consistent with the findings presented in Table 2 and Fig. 3. Fig. 4 also show the increase of oxygen containing acidic functional groups of O=C-O and C-O. The C-N content on char of FSC-400 was higher compared to that of RSC-400, which was consistent with previous research results. [46]

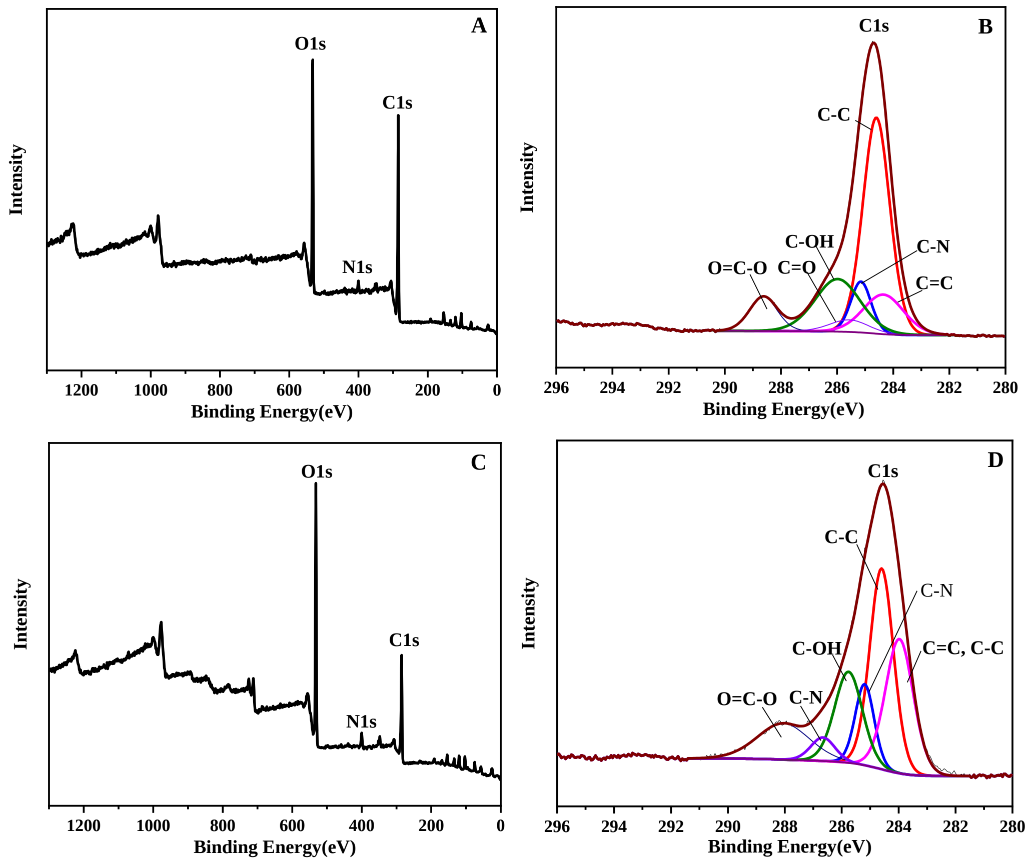
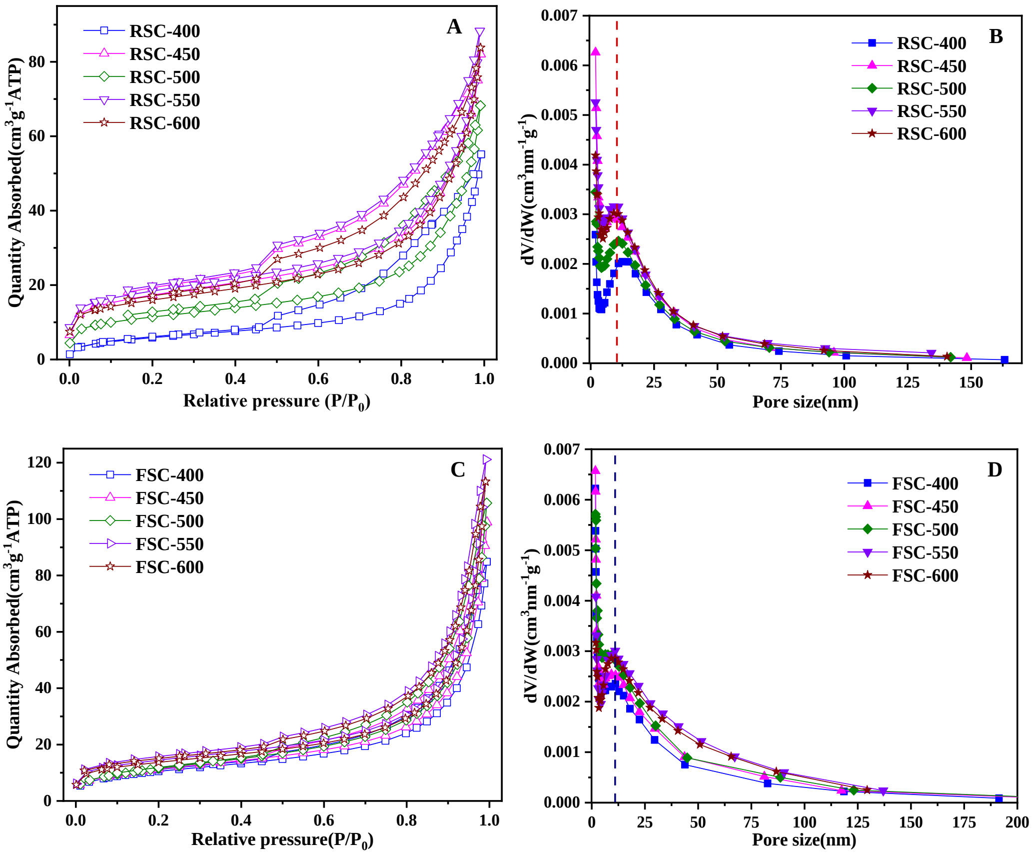


Fig. 4 A. XPS survey of RSC-400; B. Fitting spectra of C1s of RSC-400; C. XPS survey of FSC-400; D. Fitting spectra of C1s of FSC-400.

3.2.3 Effect of Fenton pre-oxidation on morphology characteristics of char

Fig. 5 provides the nitrogen isothermal adsorption profiles and pore size distributions of RSC-T and FSC-T, while Table 3 summarizes their characteristics of porosity. The micrographs of RSC-400 and FSC-400 are also displayed. According to the classification method of IUPAC, the isothermal adsorption-desorption curves of both sludge-based chars fall into class II, indicating that the adsorption of sludge-based chars was a free single multi-layer reversible adsorption process, and the chars were predominantly composed of microporous and mesoporous structures. From Fig. 5A and C, an obvious enhancement in N_2 adsorption in the relative pressure range $0 < P/P_0 < 0.99$ with carbonization temperature increasing from 400 to 550 ℃ for both chars, which is mainly attributed to the formation of the great amount of mesopores [37]. This observation is further supported by Fig. 5B and D as well as Table 3, even Fig. 5E and F. The isothermal adsorption-desorption curves revealed that the adsorption capacity of FSC-T was superior to that of RSC-T, with values of 121.13 cm^3/g and 88.30 cm^3/g, respectively. The amounts of mesopores and macropores in FSC-T were higher than those of RSC-T. As shown in Fig. 5E and F, the char obtained after pretreatment exhibited more pores compared to the FSC at 400 ℃, with a higher concentration of metallic oxide on the surface, as also observed in Fig. 3. Using the BET method, the specific surface area of each char was obtained. The variations of S_{BET} of both types of chars were found to be consistent with the observed adsorption performance in Fig. 5A and C. This correlation was further supported by the changes of the total pore volume. It is worth noting that when the temperature further went up to 600 ℃, the adsorption capacity remained almost unchanged, despite the relatively lower S_{BET}. This suggests that other factors, such as pore structure and surface chemistry, may play a significant role in the adsorption behavior of the chars at higher temperatures.



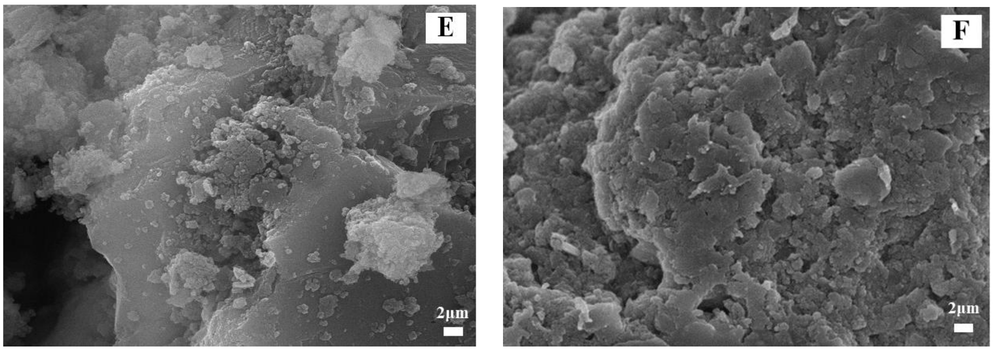


Fig. 5 A. Nitrogen isothermal adsorption profiles; B. pore size distribution of RSC-400, RSC-450, RSC-500, RSC-550 and RSC-600; C. Nitrogen isothermal adsorption profiles; D. pore size distribution of FSC-400, FSC-450, FSC-500, FSC-550 and FSC-600; E. the SEM micrograph for char of RSC-400; F. the SEM micrograph for char of FSC-400.

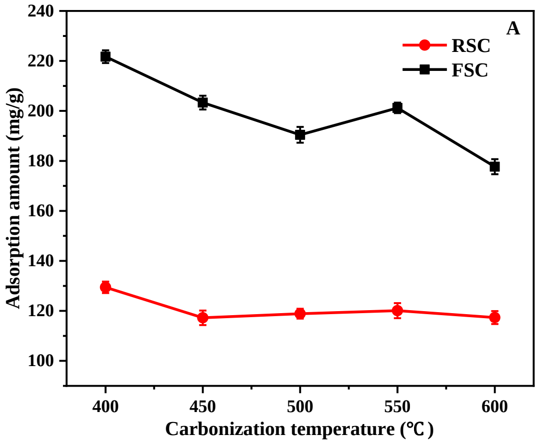
Table 3 Textural properties of sludge-based char: BET surface area, total pore volume and average pore size

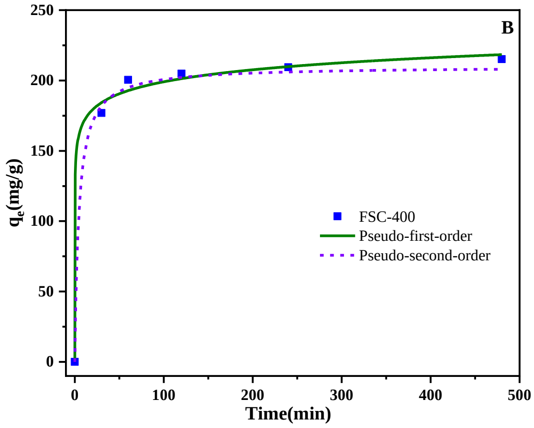
Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	P_A (nm)
RSC-400	21.12	0.085	16.40
RSC-450	40.11	0.12	15.19
RSC-500	40.85	0.10	16.19
RSC-550	48.61	0.12	15.68
RSC-600	46.08	0.12	19.70
FSC-400	37.61	0.13	14.44
FSC-450	60.41	0.15	12.39
FSC-500	61.02	0.16	14.38
FSC-550	63.61	0.18	13.17
FSC-600	55.40	0.17	13.72

3.3 Ammonia nitrogen adsorption on chars

To compare the adsorption performance of ammonia nitrogen on chars, RSC-T and FSC-T were used as adsorbents, and the dynamics models and adsorption isotherms of ammonia nitrogen adsorption on sludge-based chars were studied (Fig 6). The results indicated that the adsorption capacity of FSC-T was significantly higher than that of RSC-T. Among the tested chars, the highest adsorption capacity of chars was obtained for FSC-400, reaching approximately 221.7mg/g. As the temperature increased, the adsorption amount of FSC-400 initially continuously declined until 500 ℃, and then showed a slight increasing trend at 550 ℃. In contrast, the adsorption amounts of RSC remained relatively stable across different temperatures, with a slight decline observed from 400 to 450 ℃. This difference in behavior might be attributed to the fact that FSC-T had a higher specific surface area and more oxygenated functional groups compared to RSC-T at the same temperature, which makes FSC-T more favorable for the adsorption of ammonia nitrogen. The presence of newly formed Fe (III) and Fe (II) groups could also react with NH_4^+ in an aqueous solution, enhancing the ion exchange process. Fig. 6a further illustrates that FSC-400 had the lowest specific surface area among the FSC-T samples, while it exhibited the highest abundance of oxygenated functional groups (Fig. 3, 4 and Table 2). This observation supports the conclusion that the adsorption process is primarily governed by chemical reactions rather than physical adsorption mechanisms.

The results of the dynamics model's equations and adsorption isotherms of FSC are presented in Fig. 6 B and C, as well as Table 4 and 5. The kinetic analysis of ammonia nitrogen adsorption on FSC indicates that it followed pseudo-second-order, as evidenced by the high values of R^2 (greater than 0.9964) in Fig. 6B. The adsorption for ammonia nitrogen was rapid during the initial 80 min after which it slowed down and eventually reached a plateau with the increase of reaction time. Fig. 6C describes the adsorption isotherms of ammonia nitrogen adsorption on FSC-400. The adsorption isotherms were obtained for the ammonia nitrogen initial concentration ranging from 12.5 mg/L to 100 mg/L. The Langmuir model provided a better fit to the experimental data compared to the Freundlich model, as shown in Table 5, indicating that the adsorption process follows homogeneous monolayer adsorption. In addition, the parameter 1/n=0.7 ($0 < 0.7 < 1$) obtained from the Langmuir model indicated that the FSC was more effective in adsorbing ammonia nitrogen.





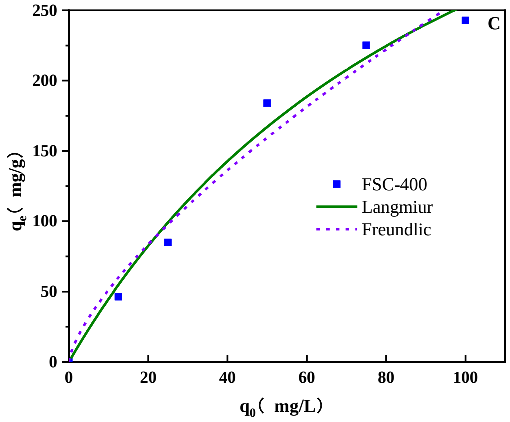


Fig.6 A. Ammonia nitrogen adsorption on sludge-based chars; B. Ammonia nitrogen isotherms on FSC-400 and dynamics fitting models; C. Ammonia nitrogen isotherms on FSC-400 and adsorption fitting models

Table 4 Parameters of adsorption dynamic model

Model	K	q_e	R^2
pseude-first-order	1.23±0.674	204.95±6.72	0.9688
pseude-second-order	0.001±1.745	209.44±5.00	0.9964

Table 5 Parameters of adsorption isotherm model

Model	K	Q/n	R^2
Langmuir	0.0082±8.7E-5	56.35±0.39	0.9959
Freundlich	10.09±4.54	1.42±0.21	0.9885

3.4 The mechanism of pre-oxidation on the adsorption properties of sludge-based char

The impact of the pre-oxidation process on FSC in this study can be summarized in four key points: Firstly, the pre-oxidation promoted the cross-linking of internal structures. The bonding conditions indicated an increase in the formation of C-C and C-N bonds. The results might be due to that the oxidation process causing further degradation of proteins, cellulose, and other substances contained in sludge. This degradation leads to the breakdown of long-chain substances, the addition of oxygen atoms, and the generation of a higher concentration of oxygen-containing groups. The oxygen-containing groups had higher reactivity than the macromolecules before oxidation, and new carbon-carbon single bonds and carbon-nitrogen double bonds were formed during the carbonization process along with the dehydration polymerization reaction [11]. Additionally, the introduction of Si-O-Si, Si-O-C and Fe-O-H occurred in FSC. These newly formed bonds were more stable and formed faster than those in RSC, and modified the reactions between the char and the ammonia nitrogen, as depicted in Fig. 7. The observed differences in bonding, compared to RSC, suggest a tendency towards cross-linking within the sludge, which can further enhance the adsorption properties of FSC for ammonia nitrogen.

Secondly, a large number of oxygen-containing groups were generated and concentrated on the surface of the char. The occurrence of the oxidation process promoted the production of oxygen-containing groups on the surface of the sludge, such as carboxyl and ester groups. As a result, it greatly enhanced the negative charge of the FSC surface, thereby greatly enhancing its ability to attract ammonia ions and improving its adsorption capacity for these ions [47].

Thirdly, the pore structure of sludge-char was also altered. The addition of oxygen-containing groups during Fenton oxidation could result in increased decarboxylation reactions during sludge carbonization. The Fenton pre-oxidation process led to the degradation of the biopolymers and the conversion of sludge flocs into small fragments [26]. This transformation has significant benefits for pore development during carbonization, as it enhanced decarboxylation reactions and caused partial destruction of the solid structure, resulting in a wider porosity. Additionally, Fenton oxidation promoted the transition from micropores to mesopores (Fig.5). As a result, the total pore volume of the char increased, and the distribution was more concentrated on mesopores [48]. These changes can enhance the capacity of FSC by improving pore filling, ion and cation exchange.

Finally, the influence of carbonization temperature on char quality was mitigated after pre-oxidation. Fenton oxidation promoted the homogenization of sludge and increased the presence of oxygen-containing groups with higher chemical reactivity. This may reduce the activation energy required during the carbonization reaction, resulting in a reduced reaction temperature for carbonization. An advanced char with relatively complete carbonization could already be obtained at 400 °C.

In summary, pre-oxidation facilitates the formation of cross-linked carbon bonds during carbonization, and the chemical properties of FSC are more advanced than those of RSC under the same reaction conditions. The oxidation process generates an abundance of oxygen-containing groups on the surface, which increases the reaction activity of the sludge and greatly reduced the activation energy required for the reaction. This also reduces the dependence of char properties on carbonization temperature. The Fenton reaction can promote a more uniformed distribution of pores in the char.

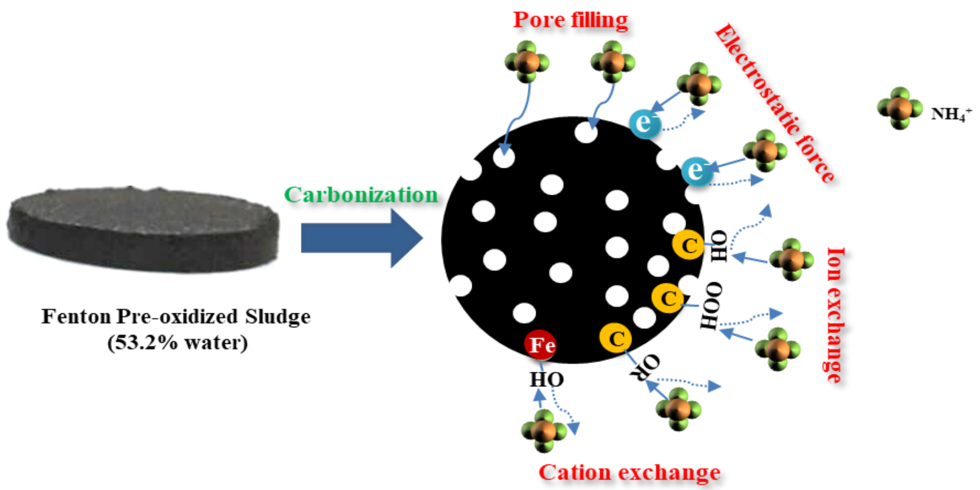


Fig.7 The adsorption mechanisms of FSC for ammonia nitrogen

3.5 Effect of Fenton pre-oxidation on sludge dewatering and sludge-based char resource utilization

Until now, the utilization of sludge in the form of char has encountered several problems: The high moisture content of sludge requires extra energy consumption because of the high energy cost of water evaporation before and during the reaction [49]; The structure of sludge-based char is usually relatively poor and often requires a high carbonization temperature or the uses of additional catalyst [47]. However, this study shows that: 1. Pre-oxidation can synchronously improve the structure and surface properties of sludge without additional consumption of materials and energy. 2. Pre-oxidation not only reduces the energy consumption associated with deep dehydration, but also lowers the energy requirement of carbonization. This approach allows for significant improvement in the char performance without major modification to the original system. 3. Integrating the dehydration and carbonization process enables better control over the quality of the final product, and adjusts the process in the dehydration and carbonization section as required to impart more unique properties to the char.

4 Conclusions

The Fenton pre-oxidation process resulted in significant surface and structural modifications of the FSC, leading to enhanced adsorption capacity for ammonia nitrogen. Compared to the RSC at the same temperature, FSC exhibited a higher abundance of functional groups on its surface. The addition of oxidants introduced new functional groups to FSC, which could react with NH_4^+ in an aqueous solution. The specific surface area and pore size distribution of FSC became larger and more uniform, facilitating improved diffusion and providing more active sites for adsorption, which is beneficial for FSC to enhance its adsorption capacity by promoting chemisorption and increasing ion interaction with ammonium ions. The adsorption capacity of ammonia nitrogen of FSC was 1.69 times higher than that of RSC, indicating the significant improvement achieved through pre-treatment. The kinetic of ammonia nitrogen adsorption on FSC followed pseudo-second-order, suggesting the involvement of both physical adsorption and chemical adsorption processes. The Langmuir model provided a better fit to the adsorption isotherm data compared to the Freundlich model, indicating that the process was characterized by homogeneous monolayer adsorption. These findings highlight the effectiveness of Fenton pre-oxidation on sludge-based char, and present it as a promising technology by integrating the dehydration and carbonization process with lower energy consumption.

CRediT authorship contribution statement

Jun Cao: Conceptualization, Investigation, Data curation, original draft. **Ruochen Wang:** Investigation, Data curation. **Hualun Zhu:** Review & Editing. **Songshan Cao:** Methodology, Review & Editing. **Zhipeng Duan:** Review & Editing.

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Effect of Fenton pre-oxidation on the physicochemical properties of Sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal

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Abstract:

Fenton pre-oxidation, as a promising technology for sludge deep dehydration, has been used intensively; however, the outputs (i.e., low-water-content sludge cakes) need to be further disposed for a full line sludge resource utilization. Carbonization presents a promising approach for disposing of the sludge cake within the process. Here, the physicochemical properties of sludge-based char obtained after Fenton pre-oxidation were studied. Both Fenton pre-oxidized sludge-based char (FSC) and raw sludge-based char (RSC) were produced within the temperature range of 400 ℃ to 600 ℃, and the adsorption performance of the prepared chars, exemplified by their ability to adsorb ammonia nitrogen (NH_4^+), was tested under various conditions. FSC exhibited superior char yield and adsorption performance compared to RSC, with chemical adsorption being the primary controlling factor. The optimum conditions for FSC were observed at 400 ℃, resulting in a char yield of 72.2%, and an adsorption capacity of 221.7 mg/g. Notably, FSC demonstrated an increase in C-C, C-N, O=C-O, C-O and C=C functional groups in comparison to RSC, which suggests that pre-oxidation increases organic matter decomposition and chemical reactivity of the sludge. The introduction of Si-O-Si, Si-O-C and Fe-O-H functional groups in the FSC facilitated ion exchange with NH_4^+ in an aqueous solution. The key findings indicate that Fenton pre-oxidation not only enhances the adsorption performance of FSC but also reduces the required carbonization temperature for excellent-char preparation. These results demonstrated the potential to integrate sludge deep dewatering, including pre-oxidation, with char preparation.

Keywords: Fenton pre-oxidation; sludge-based char; ammonia nitrogen adsorption；Surface composite modification; Structural enhancement

1 Introduction

The challenge of achieving comprehensive treatment of sludge is becoming increasingly prevalent worldwide. With the growing collection and treatment of domestic sewage in China, the country's sewage treatment capacity has significantly increased [1]. Consequently, the disposal of sewage sludge has also experienced a rapid rise, reaching approximately 60 million tons in 2020 (80% water content). There is an urgent need to develop a technology that allows for sludge recycling while minimizing its volume and associated environmental impact. However, the high moisture content of sludge, which can reach up to 99.5wt% [2], currently poses a major obstacle disposal method due to considerable energy consumption and operational costs associated with the sequent thermal conversion technologies required for further treatment of sludge. The Fenton or

Fenton-like pre-oxidation method is widely recognized as a crucial step in the pretreatment process for achieving deep water removal [3]. This method is performed prior to subsequent thermal disposal and disintegration [4, 5]. In our previous study, we modified this technology and reduced the water content from 82.5% to 53.2% under optimal conditions (mole ratio H_2O_2: Fe^{2+} =2) [6,8]. This modification effectively reduced the volume and elevated the low calorific value of the sludge. However, it resulted in the production of a significant amount of Fe-rich sludge cake, which presents challenges for proper disposal [9]. The obtained sludge cake typically retains a significant amount of organic matter, making it a key research focus to develop sustainable treatment methods in line with the goals of “emission peak” and “carbon neutralization”.

Sludge carbonization is widely regarded as a promising method to accomplish this objective [10,12]. Carbonization can greatly reduce the weight and volume by decomposing and evaporating water, while simultaneously facilitating energy conservation and the acquisition of byproducts. Sludge-based char, due to its large specific surface area, well-developed microstructure, and abundant oxygen functional groups and aromatic compounds on the surface, exhibits characteristics of both an energy material and an adsorbent. Currently, the char finds significant applications in various fields, including fuel energy, environmental protection, materials and agriculture [3, 13,16]. An important utilization of char involves its ability to adsorb and immobilize heavy metal ions [17], as well as nitrogen, phosphorus and organics in water purification, hereby acting as a cost-effective alternative to commercial adsorbents [18]. The potential for widespread application and expansion of the means depends on whether the char prepared from pre-oxidized sludge has a high utilization value. Studies have demonstrated that the Fenton and Fenton-like char synthesized by carbonization exhibits superior performance compared to that of RS, making them efficient adsorbents for pollutant removal [19]. Until now, studies have investigated the effects of temperature, residence time, preparation materials and additives on the structural characteristics of chars [20,25]. Lin et al. and Li et al. found that Fenton conditioning greatly enhanced the adsorption capacity by affecting the porosity of the sludge [26, 27]. Belete et al. reported that the Fenton reagents increased the acidic group's concentration and the BET surface area, but without changing the morphology [28]. However, our study contributes to the existing body of knowledge by exploring the relatively limited discussions on the impact of Fenton pre-oxidation on the physicochemical properties of char surfaces and its subsequent effects on the adsorption mechanism.

In aquatic environment, excessive emission of ammonia nitrogen is a significant contributor to eutrophication, posing a threat to water resources worldwide [29]. This issue has garnered global attention and has become a hot topic of concern. Consequently, the discharge standards of ammonia nitrogen have become increasingly stringent both domestically and internationally, and the efficient removal of ammonia nitrogen from water has become a crucial objective in safeguarding aquatic environment. The biochar derived from rice straw, wheat straw, coconut shell, and other materials has been identified as a simple and low-cost adsorbent for ammonia nitrogen removal from water [30]. This is due to its large specific surface area, strong ion exchange ability, and the presence of a negative charge on the surface. Previous studies have shown that there are more oxygenated functional groups formed, and the newly Fe (III) and Fe (II) groups introduced on the Fenton and Fenton-like char. These groups may enhance the ion exchange and provide an increased number of negative charges during the adsorption process [9, 19]. Considering these findings, the removal of ammonia nitrogen using Fenton pre-oxidized sludge-based char has been identified as a potential application direction due to the favorable characteristics of the char for this purpose.

Above all, in order to evaluate the mechanism of pre-oxidation on the adsorption properties of sludge-based char, both Fenton pre-oxidized sludge (FS) and the raw sludge (RS) were used to produce chars under different carbonization temperatures and residence times. The influences of Fenton pre-oxidation on char yield, element composition, specific surface area, microstructure, and functional groups were analyzed. Furthermore, the adsorption performance of ammonia nitrogen on the char and the corresponding adsorption mechanism were also studied.

2 Materials and methods

2.1 Materials

Municipal Sludge samples were collected from Xushe Wastewater Treatment Plant located in Yixing city, China. The plant has a sewage treatment capacity of 10,000 tons per day. The plant employs the A^2O+filter processing system for municipal wastewater treatment. The RS was obtained from the secondary sedimentation tank, with a moisture content of 82.5%. The FS was prepared following the procedures and the optimum conditions obtained in our previous study [7]. The mole ratio H_2O_2: Fe^{2+} was 2. The content of catalyst $FeSO_4 \cdot 7H_2O$ was 6% (m/m), and the concentration of oxidants H_2O_2 was 30%. Under these specified conditions, the moisture content of FS was successfully reduced to 53.2%. The higher heating values (HHVs) of sludge rose with the addition of oxidants, increased from 0.06 to 7.97 MJ/kg. $FeSO_4 \cdot 7H_2O$ and H_2O_2 (30%) were both purchased from Sinopharm Chemical Reagent Co., Ltd. The samples were then crushed and screened without pre-drying before all experiments. The basic property parameters of sample RS and FS were listed in Table 1.

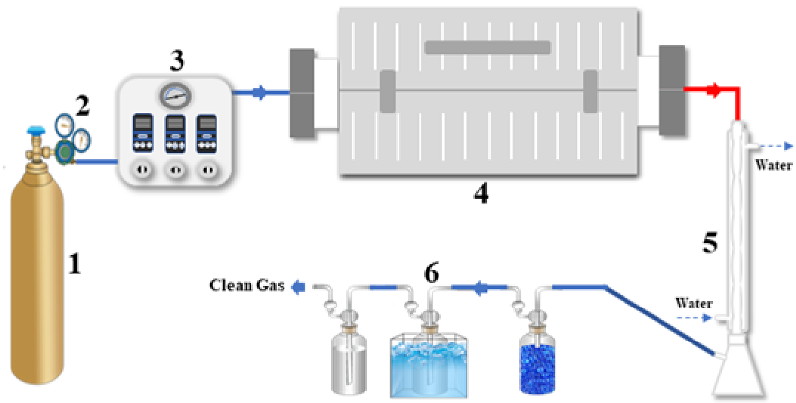
Table 1 Basic property parameters of sludge

Sample	Proximate Analysis (wt%, daf)			Elemental Analysis (%)					pH	Q_{ar}
	A_{ar}	V_{ar}	FC_{ar}	C	H	O	N	S	-	MJ▪kg^{-1}
RS	45.81	50.27	6.92	25.35	4.89	16.99	2.86	0.99	6.78	0.06
FS	42.34	51.35	3.31	23.56	4.39	18.44	3.45	1.84	4.95	7.97

2.2 Materials preparation

The sludge-based char was prepared using a system illustrated in Fig.1. An N_2 flow, which controlled by a mass flow controller, was used to maintain an inert atmosphere. The fixed bed furnace employed a quartz tube with a length of 800 mm and an inside diameter of 40 mm, heated externally by a resistance furnace controlled by a temperature programmed controller. One thermocouple was placed inside the tube to monitor the real-time temperature of the reaction zone, while the other thermocouple was set outside the tube to monitor the temperature of the reactor. The gas produced during the experiment was purified by passing it through a contented condensing device and a tail gas treatment system.

The preparation of the char proceeded as follows: First, the sludge was placed in the middle of the tube. To remove all oxygen out of the tube, N_2 was pumped-in with a flow rate of 200 ml/min for 30 min after leak checking. Then the reactor was heated at a rate of 10 °C/min, starting from room temperature to the target temperatures (400, 450, 500, 550 and 600 °C) and maintained for a certain time (30, 60, 90 and 120 min). The reactor was turned off and allowed to cool down until the furnace temperature dropped below 150 °C. Subsequently, the samples were removed from the reactor, weighted and collected. The resulting products were denoted as RSC-T and FSC-T, where T represents the target temperature. The sludge-based char yield was calculated according to the Formula 1:



1.N_2 gas cylinder; 2. Pressure reduce regulator; 3. Mass flowmeter and controller; 4. Fixed bed with electric furnace; 5. Condensing device; 6. Tail gas treatment

Fig. 1 Sludge char preparation experimental schematic diagram

$$\eta = \frac{m_0 - m_1}{m_0} \times 100\% \qquad (1)$$

where η is char yield, %; m_0 is original sludge mass, g; m_1 is mass of obtained sludge-based char, g.

2.3 Characterization and Analysis

An element analyzer (EA, EURO EA3000, Italy) was applied to determine the contents of C, H, O, N and S in sludge and char obtained at different temperatures. An acidimeter (pH, NY/T 1377.2007, China) was used to analyze the pH level and conductivity of the samples. Fourier infrared analysis (FTIR, Model Vextor 22, Germany) was conducted from 4000 to 400 cm^{-1} and each spectrum was a spectral average of at least four scans. X-ray photoelectron microscopy (XPS, Thermo Scientific ESCALAB250Xi, USA) analysis was performed and the binding energy was corrected by contaminated char (C1s, 284.6eV). The CasaXPS program was used to fit and divide peaks. The N_2 isotherm adsorption profile was obtained using an automated gas sorption analyzer (ASAP2020, Micomeritics, USA) at 77K. The specific surface areas (S_{BET}) of samples were calculated according to the Brunauer, Emmett, Teller method (BET) from the adsorption isotherms. The pore size (P_A) distribution of samples before and after calcination was calculated from desorption branch using the Barrett, Joyner and Halenda (BJH) method. Scanning electron microscope (SEM, S4800, Japan) was used to analyze the surface morphology of chars.

2.4 Ammonia nitrogen adsorption

The adsorption experiments were conducted using a set of 50 mL centrifuge tube containing 0.1 g of sludge char and 50 mL of NH_4^+ with an initial concentration of 50 mg/L in an aqueous solution. The tubes were placed on a shaker at 20 ℃ and 120 r/min. The samples were then filtered and the residual concentration of NH_4^+ was analyzed using 420 nm of Nessler reagent spectrophotometry. The adsorption capacity of NH_4^+ was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m_1} \quad (2)$$

Where, q_e represents the adsorption amount per unit mass of sludge char at adsorption equilibrium, mg/g. C_0 and C_e represent the initial and equilibrium concentrations of NH_4^+ in solution respectively, mg/L. V represents the volume of solution, mL.

For the adsorption kinetic study, a NH_4^+ solution with 50 mg/L initial concentration was applied. The behavior of the adsorption with the function of time was fitted using the pseudo-first-order (3) and pseudo-second-order (4) model [31], as followed:

$$q_t = q_e(1 - e^{-K_1 t}) \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where, t represents reaction time, min. q_t represents the sorption capacity at t time, mg/g. K_1 and K_2 represent rate constants of the two models, respectively, g/(mg·min).

The data were fitted to Langmuir and Freundlich model [32], the equations were as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

Linearized and obtained,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Linearized and obtained,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Where q_m represents saturated adsorption capacity, mg/g. K_L represents Langmuir adsorption constant. K_F represents the Langmuir adsorption constant. c_e represents the equilibrium mass concentration of ammonia nitrogen, mg/L. n represents the empirical constant.

3 Results and discussion

3.1 Carbonization

3.1.1 Effect of carbonization temperature

Fig. 2A showed the char production rate of RS and FS when the carbonization temperature rose from 400 to 600 ℃, the sample mass was 5 g and the residence time was 60 min. It can be observed that the char yield of FSC was higher than that of RSC at each temperature point, with the char production rate of FSC ranging from 62.4% to 72.2%, while that of RSC was 36.67% to 43.8%. Both FS and RS achieved the maximum char yield at 400 ℃, which were 72.2% and 43.8% respectively. With the increase of carbonization temperature, the yield of both FSC and RSC decreased. However, as the temperature further increased up to 500℃, the downward trend of sludge char yield became smaller and eventually stabilized at 550 ℃. This can be attributed to the decomposition of volatile components in the sludge, which is mostly completed by 500 ℃. At this point, further increase in temperature has a lesser effect on the char yield as the remaining components are more stable. The difference in char yield between FS and RS can be attributed to their disparate moisture content [33]. The RS had a moisture content of 82.5%, while the FS had a reduced moisture content of 53.2%. The lower moisture content in FS might lead to higher char yield, as moisture is vaporized during the carbonization process, resulting in a greater mass loss in RS compared to FS.

3.1.2 Effect of residence time

In the study conducted at 400 ℃, the effect of residence time on energy consumption and char yield was investigated. The experiments were performed with a sample weight of 5 g and residence times of 30, 60, 90, and 120 min. Fig. 2B shows that as the residence time extended from 30 min to 120 min, the decrease in char yield was 2% for FS and 1.4% for RS, respectively. This indicates that the decomposition of organic matter in the sludge had essentially completed within a residence time of 60 min. Further extending the residence time did not significantly affect the char yield, suggesting that the carbonization process had reached a relatively stable state in terms of char formation.

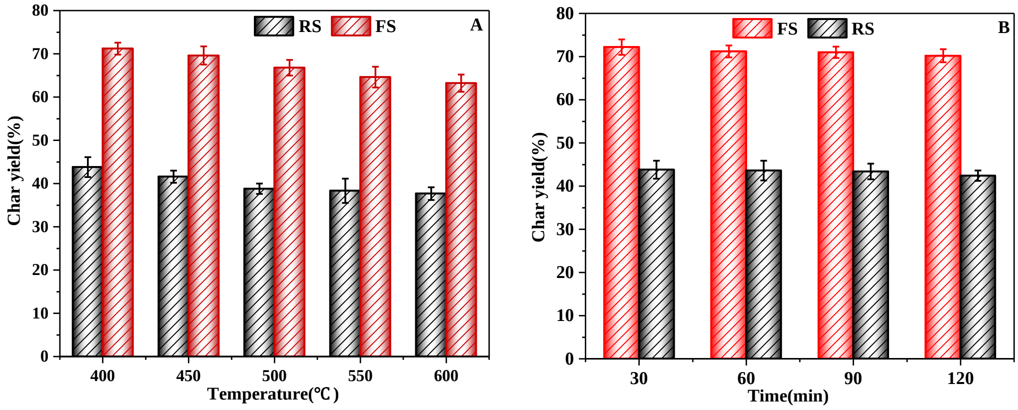


Fig. 2 A. Effect of carbonization temperature on char yield: The mass of sample was 5 g, the residence time was 60 min, the temperature was 400, 450, 500, 550, 600℃; B. Effect of residence time on char yield: The mass of sample was 5g, the temperature was 400℃ and the residence time was 30, 60, 90 and 120 min.

Above all, the carbonization temperature plays a more important role in char formation and yield than residence time, since a residence time of 60 min is sufficient to achieve optimal char yield while minimizing energy consumption.

3.2 Effect of Fenton pre-oxidation

3.2.1 Effect of Fenton pre-oxidation on elemental composition

The element composition and ash content of the char derived from different carbonization temperatures, ranging from normal atmospheric temperature to various carbonization temperatures, were carried out. The results were shown in Table 1 and Table 2. According to Table 1, the contents of ash, volatiles and S of cakes pretreated with Fenton agent were higher compared to the RS, which can be attributed to the addition of inorganic oxidants. In Table 2, it can be observed that the carbonization temperature increased, the contents of C, H, O and N, as well as the ratios of H/C, decreased for both FSC and RSC. This reduction indicated that the organic matter in the sludge was more thoroughly decomposed and released in the form of H_2O, CO_2, CO, CH_4, H_2 and NO_x with increasing temperature [4]. Thus, the content of carboxyl, hydroxyl, protein and other functional groups on the surface of char progressively decreased, indicating an increased degree of carbonization. As an important parameter to characterize the carbonization level, the decrease of H/C ratio further confirmed the enhancement of the aromaticity and stability of the char. The S content in the char showed slight growth regardless of the temperature, due to the addition of oxidants [34]. The increase of S in the char can be attributed to the addition of $FeSO_4 \cdot 7H_2O$, which exceeded the decomposition of S during the process. The O/C ratio was boosted from 0.93 for RSC-400 to 1.33 for FSC-400, and the changes of the O/C ratio could correlate with the changes of chemical functional groups including oxygen, which suggested that a surface oxidation reaction occurred during Fenton pre-oxidation, and there could be a low content of carboxylic groups on the sample surfaces [35].

Table 2 Elemental analysis and calorific value of sludge-based char

Carbonization Temperature/ ℃	Elemental analysis/%							Ash/%
T	C	H	O	N	S	H/C	O/C	-
RSC-400	17.10	1.93	15.90	2.53	0.67	0.11	0.93	61.87
RSC-450	13.15	1.37	14.17	2.01	0.97	0.10	1.08	68.33
RSC-500	12.46	1.05	12.08	1.93	0.93	0.08	0.97	71.55
RSC-550	11.31	0.85	11.43	1.66	0.84	0.08	1.01	73.91
RSC-600	11.42	0.63	10.46	1.49	0.73	0.06	0.92	75.27
FSC-400	13.41	1.70	17.90	2.24	1.53	0.13	1.33	63.12
FSC-450	12.37	1.52	17.57	2.03	1.58	0.12	1.42	64.83
FSC-500	12.14	1.31	16.26	1.84	1.65	0.11	1.34	66.7
FSC-550	11.67	1.13	15.08	1.71	1.67	0.10	1.29	68.56
FSC-600	11.72	0.97	14.24	1.59	1.55	0.08	1.22	69.44

3.2.2 Effect of Fenton pre-oxidation on surface functional groups of char

The FTIR spectra of RSC-T and FSC-T were provided in Fig. 3. An adsorption peak observed between 2300~2420 cm^{-1} may be attributed to the S-H and C-N stretching vibrations [36]. The adsorption peak around 2305~2320 cm^{-1} are due to the -COO antisymmetric stretching vibration in carboxyl group or the stretching vibration of C=O in lactone group [37]. For RS, the peak intensity was the strongest at 400 ℃. With the temperature increasing, the peak gradually disappeared, but reappeared when the temperature reached 600 ℃. The peak observed in FSC was weak when the temperature rose from 400 to 450 ℃.

However, the peak became more prominent at 500 ℃, before weakening and disappearing at 600 ℃. This suggested that the oxidation process caused a rearrangement of the functional groups in the sludge, resulting in changes in the observed peak intensity. The observed trend is consistent with the changes in the N ratio in both types of sludge. The region near 1550-1600 cm^{-1}, which only occurred in FSC-T, corresponded to the stretching vibrations of carbonyl structures of C=O and alkene of C=C bonds. This indicates that the pretreated sludge facilitates the generation of the small molecule organics and indirectly increasing C=O and C=C [38, 39]. It can be found that the surface of the sludge-based char contains various substances or functional groups such as hydroxyl, phenolic hydroxyl, carboxyl, amino, imino, lactone, anhydride, ether, ester and other substances or functional groups [40], revealing that the surface of FSC was enriched with oxygen-containing functional groups, particularly acids and aldehydes, after the pre-oxidation. The stretching vibration adsorption peaks at 1040 cm^{-1} and 976 ~ 1038 cm^{-1} can be endorsed to Si-O-Si or Si-O-C and Fe-O-H, respectively. The peaks observed in FSC-T were evidently higher than those of RSC-T, which showed that the addition of reagent ($FeSO_4 \cdot 7H_2O$) introduced new minerals. The adsorption peaks observed at 619 cm^{-1} corresponded to Si-O-Fe bonds [28, 41]. The stretching vibration adsorption peaks at 680-580 cm^{-1} corresponded to S=O and O=S=O, which are characteristic of SO_4^{2-}. The presence of these peaks suggests that sulfuric acid groups were introduced onto the surface of char [42, 43], which is consistent with the increase in S element content as shown in Table 2.

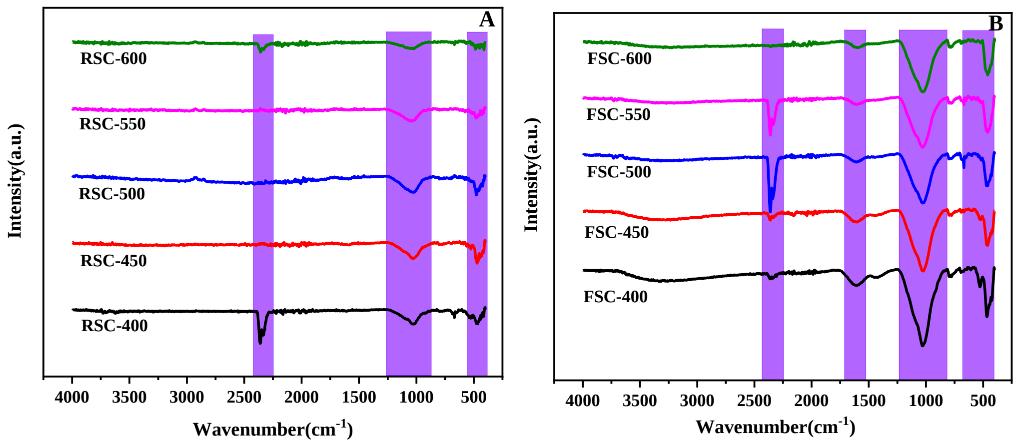


Fig. 3 A. FTIR spectra of RSC-400, RSC-450, RSC-500, RSC-550 and RSC-600; B. FTIR spectra of FSC-400, FSC-450, FSC-500, FSC-550 and FSC-600.

The effect of Fenton pre-oxidation on the carbon-containing groups on the surface of char obtained at 400 ℃ was investigated using XPS, as depicted in Fig. 4. The proportions of surface element content were analyzed and are presented in Table S1. The C1s peak of RSC-400 and FSC-400 was broken down into six peaks by Casa XPS software, representing typical sp^2 C=C (284.2 eV), sp^3 C-C\C-H (284.6 eV), C-O (285.4-286.0 eV), C-N (protein-N, 285.4eV) and O=C-O (288.2-290.2e) [44] as shown in Fig. 4. There was no similar variation pattern in the C content of the surface of RSC-T and FSC-T (Table S1). However, the C content on the surface of FSC-400 decreased compared to that of RSC-400. This might be due to the increase of O content resulting from the addition of the oxygen-containing reagent [45], this observation is consistent with the findings presented in Table 2 and Fig. 3. Fig. 4 also show the increase of oxygen containing acidic functional groups of O=C-O and C-O. The C-N content on char of FSC-400 was higher compared to that of RSC-400, which was consistent with previous research results. [46]

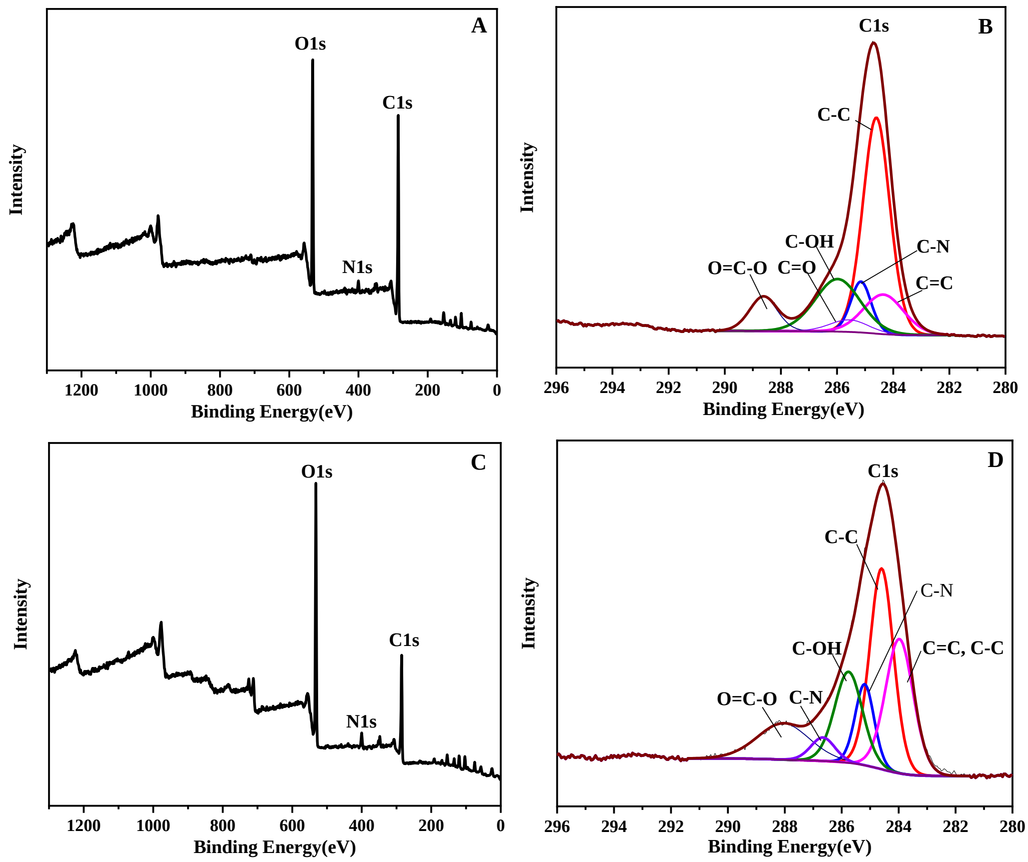
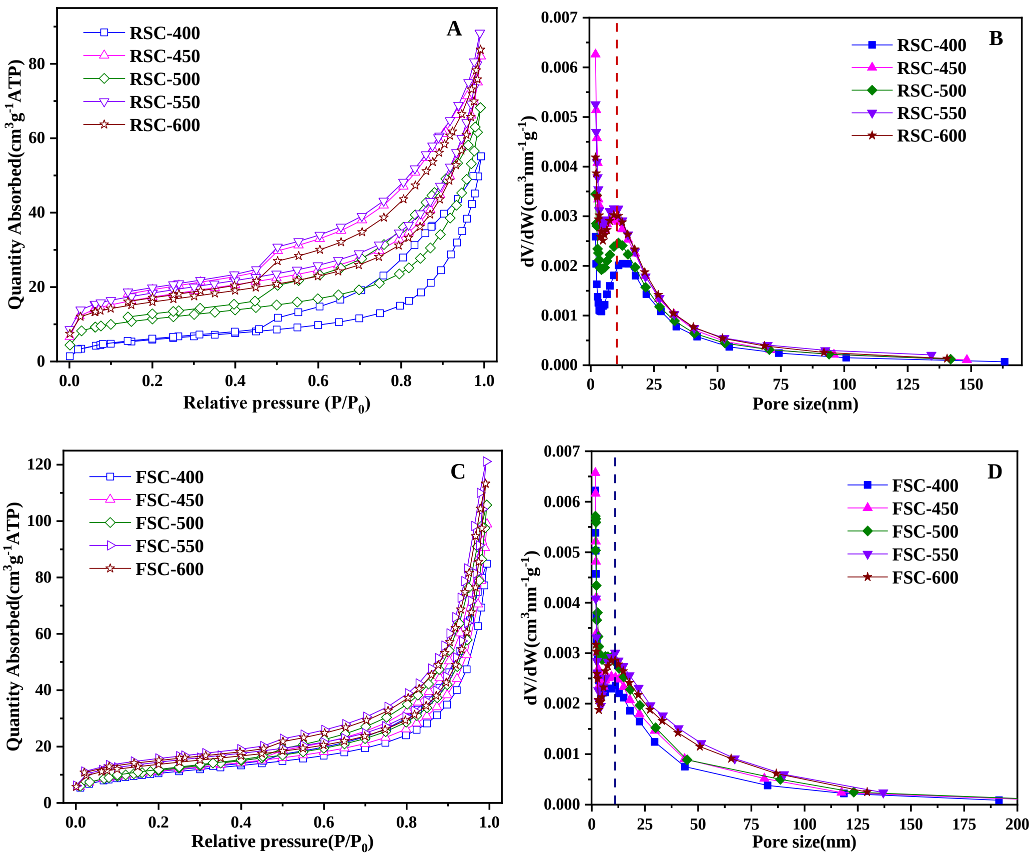


Fig. 4 A. XPS survey of RSC-400; B. Fitting spectra of C1s of RSC-400; C. XPS survey of FSC-400; D. Fitting spectra of C1s of FSC-400.

3.2.3 Effect of Fenton pre-oxidation on morphology characteristics of char

Fig. 5 provides the nitrogen isothermal adsorption profiles and pore size distributions of RSC-T and FSC-T, while Table 3 summarizes their characteristics of porosity. The micrographs of RSC-400 and FSC-400 are also displayed. According to the classification method of IUPAC, the isothermal adsorption-desorption curves of both sludge-based chars fall into class II, indicating that the adsorption of sludge-based chars was a free single multi-layer reversible adsorption process, and the chars were predominantly composed of microporous and mesoporous structures. From Fig. 5A and C, an obvious enhancement in N_2 adsorption in the relative pressure range $0 < P/P_0 < 0.99$ with carbonization temperature increasing from 400 to 550 ℃ for both chars, which is mainly attributed to the formation of the great amount of mesopores [37]. This observation is further supported by Fig. 5B and D as well as Table 3, even Fig. 5E and F. The isothermal adsorption-desorption curves revealed that the adsorption capacity of FSC-T was superior to that of RSC-T, with values of 121.13 cm^3/g and 88.30 cm^3/g, respectively. The amounts of mesopores and macropores in FSC-T were higher than those of RSC-T. As shown in Fig. 5E and F, the char obtained after pretreatment exhibited more pores compared to the FSC at 400 ℃, with a higher concentration of metallic oxide on the surface, as also observed in Fig. 3. Using the BET method, the specific surface area of each char was obtained. The variations of S_{BET} of both types of chars were found to be consistent with the observed adsorption performance in Fig. 5A and C. This correlation was further supported by the changes of the total pore volume. It is worth noting that when the temperature further went up to 600 ℃, the adsorption capacity remained almost unchanged, despite the relatively lower S_{BET}. This suggests that other factors, such as pore structure and surface chemistry, may play a significant role in the adsorption behavior of the chars at higher temperatures.



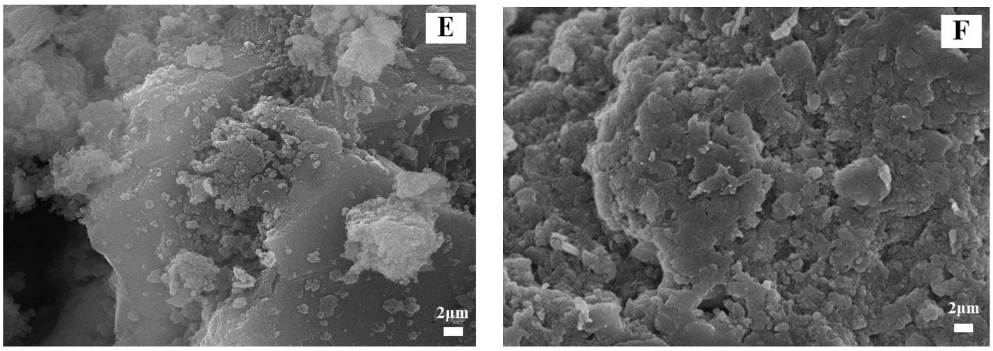


Fig. 5 A. Nitrogen isothermal adsorption profiles; B. pore size distribution of RSC-400, RSC-450, RSC-500, RSC-550 and RSC-600; C. Nitrogen isothermal adsorption profiles; D. pore size distribution of FSC-400, FSC-450, FSC-500, FSC-550 and FSC-600; E. the SEM micrograph for char of RSC-400; F. the SEM micrograph for char of FSC-400.

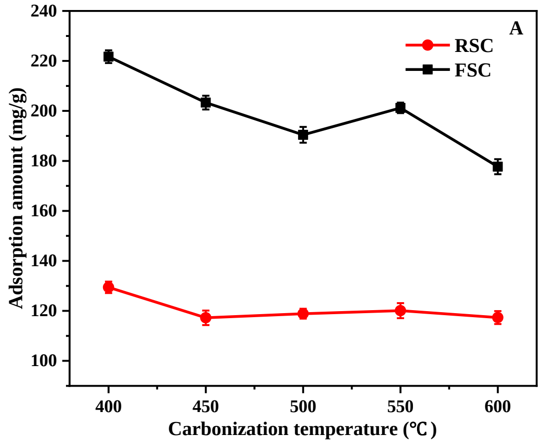
Table 3 Textural properties of sludge-based char: BET surface area, total pore volume and average pore size

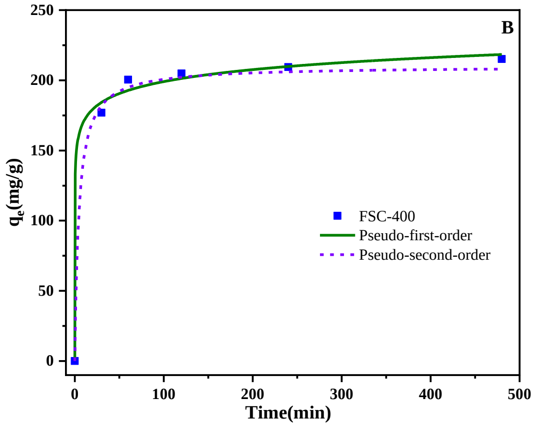
Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	P_A (nm)
RSC-400	21.12	0.085	16.40
RSC-450	40.11	0.12	15.19
RSC-500	40.85	0.10	16.19
RSC-550	48.61	0.12	15.68
RSC-600	46.08	0.12	19.70
FSC-400	37.61	0.13	14.44
FSC-450	60.41	0.15	12.39
FSC-500	61.02	0.16	14.38
FSC-550	63.61	0.18	13.17
FSC-600	55.40	0.17	13.72

3.3 Ammonia nitrogen adsorption on chars

To compare the adsorption performance of ammonia nitrogen on chars, RSC-T and FSC-T were used as adsorbents, and the dynamics models and adsorption isotherms of ammonia nitrogen adsorption on sludge-based chars were studied (Fig 6). The results indicated that the adsorption capacity of FSC-T was significantly higher than that of RSC-T. Among the tested chars, the highest adsorption capacity of chars was obtained for FSC-400, reaching approximately 221.7mg/g. As the temperature increased, the adsorption amount of FSC-400 initially continuously declined until 500 ℃, and then showed a slight increasing trend at 550 ℃. In contrast, the adsorption amounts of RSC remained relatively stable across different temperatures, with a slight decline observed from 400 to 450 ℃. This difference in behavior might be attributed to the fact that FSC-T had a higher specific surface area and more oxygenated functional groups compared to RSC-T at the same temperature, which makes FSC-T more favorable for the adsorption of ammonia nitrogen. The presence of newly formed Fe (III) and Fe (II) groups could also react with NH_4^+ in an aqueous solution, enhancing the ion exchange process. Fig. 6a further illustrates that FSC-400 had the lowest specific surface area among the FSC-T samples, while it exhibited the highest abundance of oxygenated functional groups (Fig. 3, 4 and Table 2). This observation supports the conclusion that the adsorption process is primarily governed by chemical reactions rather than physical adsorption mechanisms.

The results of the dynamics model's equations and adsorption isotherms of FSC are presented in Fig. 6 B and C, as well as Table 4 and 5. The kinetic analysis of ammonia nitrogen adsorption on FSC indicates that it followed pseudo-second-order, as evidenced by the high values of R^2 (greater than 0.9964) in Fig. 6B. The adsorption for ammonia nitrogen was rapid during the initial 80 min after which it slowed down and eventually reached a plateau with the increase of reaction time. Fig. 6C describes the adsorption isotherms of ammonia nitrogen adsorption on FSC-400. The adsorption isotherms were obtained for the ammonia nitrogen initial concentration ranging from 12.5 mg/L to 100 mg/L. The Langmuir model provided a better fit to the experimental data compared to the Freundlich model, as shown in Table 5, indicating that the adsorption process follows homogeneous monolayer adsorption. In addition, the parameter 1/n=0.7 (0 < 0.7 < 1) obtained from the Langmuir model indicated that the FSC was more effective in adsorbing ammonia nitrogen.





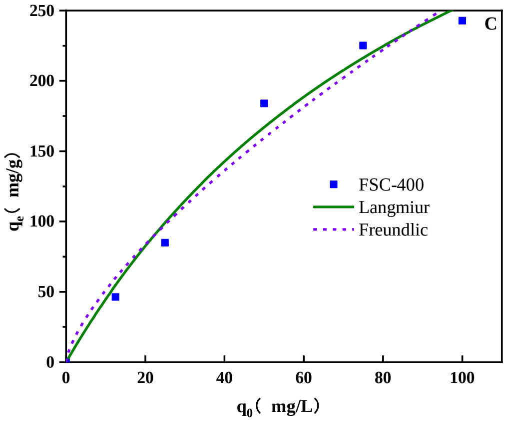


Fig.6 A. Ammonia nitrogen adsorption on sludge-based chars; B. Ammonia nitrogen isotherms on FSC-400 and dynamics fitting models; C. Ammonia nitrogen isotherms on FSC-400 and adsorption fitting models

Table 4 Parameters of adsorption dynamic model

Model	K	q_e	R^2
pseude-first-order	1.23±0.674	204.95±6.72	0.9688
pseude-second-order	0.001±1.745	209.44±5.00	0.9964

Table 5 Parameters of adsorption isotherm model

Model	K	Q/n	R^2
Langmuir	0.0082±8.7E-5	56.35±0.39	0.9959
Freundlich	10.09±4.54	1.42±0.21	0.9885

3.4 The mechanism of pre-oxidation on the adsorption properties of sludge-based char

The impact of the pre-oxidation process on FSC in this study can be summarized in four key points: Firstly, the pre-oxidation promoted the cross-linking of internal structures. The bonding conditions indicated an increase in the formation of C-C and C-N bonds. The results might be due to that the oxidation process causing further degradation of proteins, cellulose, and other substances contained in sludge. This degradation leads to the breakdown of long-chain substances, the addition of oxygen atoms, and the generation of a higher concentration of oxygen-containing groups. The oxygen-containing groups had higher reactivity than the macromolecules before oxidation, and new carbon-carbon single bonds and carbon-nitrogen double bonds were formed during the carbonization process along with the dehydration polymerization reaction [11]. Additionally, the introduction of Si-O-Si, Si-O-C and Fe-O-H occurred in FSC. These newly formed bonds were more stable and formed faster than those in RSC, and modified the reactions between the char and the ammonia nitrogen, as depicted in Fig. 7. The observed differences in bonding, compared to RSC, suggest a tendency towards cross-linking within the sludge, which can further enhance the adsorption properties of FSC for ammonia nitrogen.

Secondly, a large number of oxygen-containing groups were generated and concentrated on the surface of the char. The occurrence of the oxidation process promoted the production of oxygen-containing groups on the surface of the sludge, such as carboxyl and ester groups. As a result, it greatly enhanced the negative charge of the FSC surface, thereby greatly enhancing its ability to attract ammonia ions and improving its adsorption capacity for these ions [47].

Thirdly, the pore structure of sludge-char was also altered. The addition of oxygen-containing groups during Fenton oxidation could result in increased decarboxylation reactions during sludge carbonization. The Fenton pre-oxidation process led to the degradation of the biopolymers and the conversion of sludge flocs into small fragments [26]. This transformation has significant benefits for pore development during carbonization, as it enhanced decarboxylation reactions and caused partial destruction of the solid structure, resulting in a wider porosity. Additionally, Fenton oxidation promoted the transition from micropores to mesopores (Fig.5). As a result, the total pore volume of the char increased, and the distribution was more concentrated on mesopores [48]. These changes can enhance the capacity of FSC by improving pore filling, ion and cation exchange.

Finally, the influence of carbonization temperature on char quality was mitigated after pre-oxidation. Fenton oxidation promoted the homogenization of sludge and increased the presence of oxygen-containing groups with higher chemical reactivity. This may reduce the activation energy required during the carbonization reaction, resulting in a reduced reaction temperature for carbonization. An advanced char with relatively complete carbonization could already be obtained at 400 °C.

In summary, pre-oxidation facilitates the formation of cross-linked carbon bonds during carbonization, and the chemical properties of FSC are more advanced than those of RSC under the same reaction conditions. The oxidation process generates an abundance of oxygen-containing groups on the surface, which increases the reaction activity of the sludge and greatly reduced the activation energy required for the reaction. This also reduces the dependence of char properties on carbonization temperature. The Fenton reaction can promote a more uniformed distribution of pores in the char.

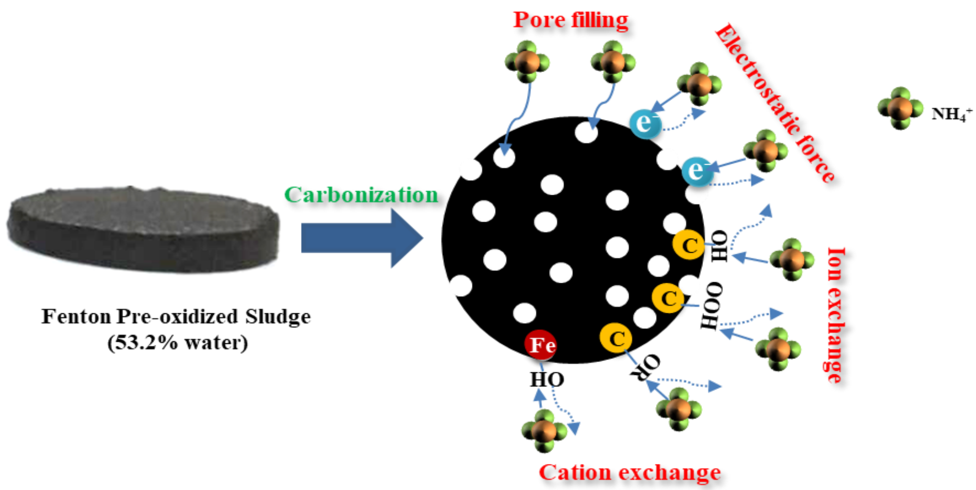


Fig.7 The adsorption mechanisms of FSC for ammonia nitrogen

3.5 Effect of Fenton pre-oxidation on sludge dewatering and sludge-based char resource utilization

Until now, the utilization of sludge in the form of char has encountered several problems: The high moisture content of sludge requires extra energy consumption because of the high energy cost of water evaporation before and during the reaction [49]; The structure of sludge-based char is usually relatively poor and often requires a high carbonization temperature or the uses of additional catalyst [47]. However, this study shows that: 1. Pre-oxidation can synchronously improve the structure and surface properties of sludge without additional consumption of materials and energy. 2. Pre-oxidation not only reduces the energy consumption associated with deep dehydration, but also lowers the energy requirement of carbonization. This approach allows for significant improvement in the char performance without major modification to the original system. 3. Integrating the dehydration and carbonization process enables better control over the quality of the final product, and adjusts the process in the dehydration and carbonization section as required to impart more unique properties to the char.

4 Conclusions

The Fenton pre-oxidation process resulted in significant surface and structural modifications of the FSC, leading to enhanced adsorption capacity for ammonia nitrogen. Compared to the RSC at the same temperature, FSC exhibited a higher abundance of functional groups on its surface. The addition of oxidants introduced new functional groups to FSC, which could react with NH_4^+ in an aqueous solution. The specific surface area and pore size distribution of FSC became larger and more uniform, facilitating improved diffusion and providing more active sites for adsorption, which is beneficial for FSC to enhance its adsorption capacity by promoting chemisorption and increasing ion interaction with ammonium ions. The adsorption capacity of ammonia nitrogen of FSC was 1.69 times higher than that of RSC, indicating the significant improvement achieved through pre-treatment. The kinetic of ammonia nitrogen adsorption on FSC followed pseudo-second-order, suggesting the involvement of both physical adsorption and chemical adsorption processes. The Langmuir model provided a better fit to the adsorption isotherm data compared to the Freundlich model, indicating that the process was characterized by homogeneous monolayer adsorption. These findings highlight the effectiveness of Fenton pre-oxidation on sludge-based char, and present it as a promising technology by integrating the dehydration and carbonization process with lower energy consumption.

CRediT authorship contribution statement

Jun Cao: Conceptualization, Investigation, Data curation, original draft. **Ruochen Wang:** Investigation, Data curation. **Hualun Zhu:** Review & Editing. **Songshan Cao:** Methodology, Review & Editing. **Zhipeng Duan:** Review & Editing.

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