


Evaluation of omphacite and iron-coated omphacite as a water filtration medium

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ABSTRACT

In this study, omphacite medium were modified by roasting at high temperature. The optimal preparation conditions were as follows: the pH value was 1, concentration of FeCl_3 was 2 mol/L, roasting temperature was 450 °C and roasting time was 2 h. Specific surface area, scanning electron microscopy, and EDS analysis were used to compare the unmodified and modified omphacite, and a dynamic filtration experiment was performed to treat the slightly polluted water. The analysis of the characterization results revealed that the surface structure of the modified omphacite filter medium changed greatly. Its surface was rough and potholes increased, and the specific surface area and adsorption capacity were significantly increased. Results of the dynamic filtration experiment revealed that the average removal efficiencies of organic matter, TOC, and turbidity by quartz sand were 21.17%, 2.2%, and 94.5%. The average removal efficiencies of organic matter, TOC, and turbidity by unmodified omphacite were 23.46%, 26.7%, and 95.2%. The average removal efficiencies of organic matter, TOC, and turbidity by modified omphacite were 50.35%, 45.5%, and 96.3%. On the whole, the filtration performance of the modified omphacite filter column was the best among the three filter columns, and the recovery of the backwashing performance was also better.

Key words: backwash, dynamic filter, filtration, modified omphacite medium

HIGHLIGHTS

- In this paper, the principle of good filtration performance of modified omphacite was studied comprehensively by combining characterization methods with dynamic filtration experiment.
- The study of omphacite as water treatment filter medium in this paper is the intersection of mineral processing and environmental science.
- The development of omphacite filtration technology can not only provide new market hot spots for minerals in the East China Sea area, but also has a very positive value for improving water treatment technology and enhancing water treatment efficiency.

1. INTRODUCTION

In recent years, with the accelerating pace of China's industrialization, harmful substances in water have been increasing, and the degree of water pollution has become increasingly serious, especially in river water. The Yangtze River, Yellow River, Pearl River, Songhua River, Huaihe River, Haihe River, Liaohe River, and some rivers in the provinces of Zhejiang and Fujian and the interior and southwest of China belong to ten large water system control sections in 469 state-controlled regions, with I–III class, IV–V class, and substandard V class cross-section ratios of 61.0%, 25.3%, and 13.7%, respectively (Jin *et al.* 2019). With the increase in standards of living, the quality of life of people is gradually improving, and people have also improved the quality of their drinking water. On the one hand, water sources throughout the country are seriously polluted. On the other hand, societal sanitary requirements for drinking water are continuously increasing (He 2012). These two aspects have greatly enhanced the water quality requirements for the effluent from waterworks.

At present, China's drinking water treatment technology is based on conventional technology, that is, coagulation–sedimentation–filtration–disinfection. Owing to the full use of existing process facilities, enhancement of the conventional process has the benefits of low investment, high speed, and high effectiveness, which are suitable for the current situation of water treatment in China (Zuo 2012). Therefore, strengthening the conventional drinking water treatment process has become a popular research topic. Filter medium can directly affect effluent water quality, so filter efficiency and economy

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are largely determined by their properties (Pantelev *et al.* 2020). Research and development of filter medium that are better than the traditional filter medium can result in improvements in the water production process of the whole water plant and the effluent water quality (Deng *et al.* 2001). At home and abroad, the modified filter medium are obtained by covering a variety of natural filter medium with the modifier through chemical reactions. Commonly used modifiers include ferric hydroxide, ferric oxide, aluminum hydroxide, and alumina; commonly used natural filter medium include ordinary quartz sand, and zeolite (Lv *et al.* 2020). A new type of iron oxide modified sand filter medium studied by scholars such as Liu *et al.* (2014) was roasted at high temperature by adding a FeCl_3 modifier on the basis of ordinary quartz sand. Studies showed that a layer of biofilm is firmly attached to the surface of the modified sand, increasing its specific surface area, and functions such as physical adsorption and biological oxidation enable it to have a high removal efficiency for ammonia nitrogen and organic matter. Huang *et al.* (2020) focused on the preparation of a novel adsorbent from coal fly ash (CFA) and solid alkali (NaOH) by the low-temperature roasting method. They found that in the new adsorbent with a mass ratio of CFA and NaOH 5:8, calcination temperature of 300 °C or 350 °C, and reaction time of 3 h, the novel adsorbent had the best adsorption capacities and accorded with the Langmuir isotherm and the pseudo-second-order kinetic models. Wang *et al.* (2010) used PAC to modify quartz sand filter medium. Studies showed that the removal effect of PAC modified quartz sand filter medium on COD_{Mn} and UV_{254} is better than that of ordinary quartz sand filter medium without modification. The surface structure and isoelectric point of the filter medium modified by PAC changed, improving the removal effect for natural organic matter. To effectively remove bacteria from stormwater, Li *et al.* (2014) developed a stable type of Cu-zeolite medium by modifying ZCu through calcination and *in situ* $\text{Cu}(\text{OH})_2$ coating, achieving considerable improvement.

At present, general water treatment plant filter medium are mostly ordinary quartz sand filter medium. A small number of water plants also use ceramic, anthracite, fiber ball, and activated carbon filter medium. However, due to the limitations of these filter medium themselves (such as their limited specific surface area, negative surface charge under neutral pH conditions, or expensiveness), people began attempting to find an economical and good filtering effect from modified filter medium (Yi & Deng 2000). In the process of China's economic development, most projects have involved mineral resources, but their actual utilization efficiency is low, with nearly 80% of the medium being tailings. The emergence of tailings not only causes a serious waste of resources but also pollutes the environment and presents many potential safety risks, limiting the construction of an environment-friendly society (Deng & Chen 2015). Eclogite-type rutile resources in China are mainly distributed in the Dabieshan-Su-Lu hypersonic high-pressure metamorphic zone, in a zonal distribution from Rongcheng of Shandong Province to the East China Sea of Jiangsu Province, and from Yuexi of Anhui Province to Xinxian of Henan Province (Xu & Xu 2009). Omphacite shows relatively high aspect ratios, a low angle between the long axes of crystals and the foliation, a wide grain-size distribution, and distinctive CPOs, suggesting that dislocation creep is the main deformation mechanism (Kim *et al.* 2018). The development of the omphacite filtration process can not only provide a new market focus in the comprehensive utilization of tailings and the improvement of resource utilization efficiency but also results in a very positive value for the improvement of the water treatment process and the enhancement of water treatment efficiency.

In this study, omphacite produced by Lianyungang Mining was used as a filter medium. The omphacite medium was modified by roasting at high temperature using FeCl_3 as a modifier. The dynamic filtration experiment was carried out to study the medium's performance in filtration and backwashing with quartz sand, unmodified omphacite, and modified omphacite filter medium. The purpose of this paper is to study the possibility of modified omphacite as a new filter medium for water treatment.

2. MATERIALS AND METHODS

2.1. Materials

Omphacite was obtained from a mineral company in Jiangsu. Quartz sand was collected from a water plant in Jiangsu. Humic acid was purchased from Aladdin Reagents Co., Ltd (Shanghai, China). Concentrated sulfuric acid (H_2SO_4), concentrated hydrochloric acid (HCl), and sodium hydroxide (NaOH) were all purchased from Nanjing Chemical Reagent Co., Ltd (Nanjing, China). Iron trichloride (FeCl_3) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Filtration medium

Omphacite, a member of the pyroxene group of silicate minerals, had particle size $\Phi = 0.8\text{--}1.2$ mm, effective particle density $\rho = 3.35$ g/m³, porosity $e = 49.5\%$, effective diameter $d_{10} = 0.76$ mm, and non-uniform coefficient

$K_{80} = d_{80}/d_{10} = 1.12/0.76 = 1.47$; quartz sand had particle size $\Phi = 0.5\text{--}1.2$ mm, porosity $e = 41\%$, effective diameter $d_{10} = 0.60$ mm, specific surface area $S = 0.15 \times 10^4$ cm²/g.

2.3. Preparation of modified omphacite medium

The filter medium with 0.80–1.2 mm particle size was screened by screen cloth and rinsed repeatedly with clean water to remove surface dust. Given that most of the oxides are soluble in either acid or alkali, alkaline soaking and acid soaking methods are used to pretreat omphacite to remove its surface impurities. After rinsing, the medium was immersed in a 1 mol/L sodium hydroxide solution for 24 h and rinsed again until pH was neutral. Then, it was immersed in a 1 mol/L hydrochloric acid solution for 24 h, rinsed with distilled water and placed into a 105 °C oven for drying. Finally, the omphacite medium was cooled to room temperature and then modified.

The commonly used methods of filter medium modification are high-temperature roasting, repeated sedimentation, and coating. Zhao *et al.* (2007) compared the removal effect of modified quartz sand made by different modification methods on organic matter and concluded that the quartz sand modified by the high-temperature roasting method has the best effect in removing organic matter. Thus, this paper chose the high-temperature roasting method. In the high-temperature roasting method, a metal brine solution is heated to produce hydroxide precipitation, which is then transformed into metal oxides and attached to the surface of the filter medium.

The 200 g of pretreated omphacite medium was divided into five parts, each of which was 40 g, and prepared under different conditions. The single factors were the pH value, concentration of FeCl₃, roasting temperature and roasting time. Then, 100 ml humic acid solution of 20 mg/L was added into beakers respectively, and the beakers were shaken at a speed of 100 r/min for 3 h. After standing for 1 h, the supernatant in the beakers was taken to measure the UV₂₅₄ value. The removal efficiencies of UV₂₅₄ were measured to determine the optimal preparation conditions.

2.4. Surface characteristics of modified omphacite medium

The density and porosity of omphacite medium before and after modification were measured and calculated to reflect its compactness. The density of the filter medium was measured as follows. A total of 100 ml distilled water was added to the 200 ml measuring cylinder, $V_1 = 100$ ml. Then, 100 g modified omphacite filter medium, which was dried and cooled, was added to the measuring cylinder. The reading obtained at this time was marked as V_2 . The density of the filter medium is obtained from the following calculation:

$$\rho = \frac{G}{V_2 - V_1}$$

The modified omphacite filter medium obtained in the previous step was filtered and washed with distilled water, and the volume V_3 was measured by repeating the above steps. The porosity of the filter medium is obtained from the following calculation:

$$m = 1 - \frac{G}{\rho V_3}$$

The specific surface area of the omphacite medium before and after modification was measured by the BET specific surface area method (BET, 3H-2000PS1, China).

The changes in surface conditions of the omphacite medium before and after modification were analyzed by scanning electron microscopy (SEM, JSM-6510, USA).

The content changes of the main elements in the omphacite medium before and after modification were analyzed by an EDS energy spectrometer (EDS, NS7, USA).

2.5. Study on the stability of modified omphacite medium

After modification, the surface of the omphacite filter medium was covered with iron oxide. To ensure the adhesion strength of iron oxide in the filtration process, the physical and chemical stability of the modified filter medium was evaluated by the shedding of the iron on the medium surface under high washing strength and an acid-base environment. The specific methods were as follows. (1) Physical stability measurement: 100 g of modified omphacite filter medium was weighed and then placed

in a filter column with an inner diameter of 20 mm and a height of 1.2 m, then washed continuously for 24 h in $12 \text{ L/s}\cdot\text{m}^2$ of high washing intensity. The changes in iron content before and after washing were measured by phenanthroline spectrophotometry. (2) Chemical stability measurement: two samples of 1 g modified omphacite filter medium were weighed, respectively immersed in 100 ml, $\text{pH} = 3$ hydrochloric acid solution and $\text{pH} = 12$ sodium hydroxide solution, and shaken at a speed of 180 r/min for 24 h. The changes in iron content on the surface of the filter medium before and after the reaction were measured by phenanthroline spectrophotometry.

2.6. Dynamic filtration experiment

The experimental device is illustrated in Figure 1. In this experiment, the length, width, and height of the raw water tank are 0.8, 0.5, and 0.9 m, respectively. The volume is 0.36 m^3 . The raw water configured is lifted by the pump and then enters the filter column. Two filter columns are used in this experiment, all of which are made of Plexiglas and have a diameter of 100 mm and have a height of 2,500 mm. The middle part of the filter column is connected by a flange, which is convenient for disassembly in replacing the filter medium. The bottom end of the filter column is connected to the fixed tripod by welding. The top part of the filter column is provided with an inlet pipe and backwashing drain pipe with respective diameters of 20 and 50 mm. The bottom of the filter column is provided with a backwashing inlet pipe with a diameter of 20 mm. The inorganic raw water was configured by campus clay and tap water, and the organic raw water was configured by humic acid and water in the experiment. The experimental conditions were as follows. Turbidity of influent water was $15.75 \pm 4.12 \text{ NTU}$, UV_{254} was $0.31 \pm 0.043 \text{ cm}^{-1}$, the dosage of humic acid was 10 mg/L.

The filter medium were loaded into filter columns with a thickness of 850 mm. The filtration method was direct filtration with a fixed filtration rate of 8 m/h. Poly aluminum chloride (PAC) was selected as flocculant. The turbidity of the influent water was $15.75 \pm 4.12 \text{ NTU}$, which was relatively low, and the flocculant only played an auxiliary role in the filtration stage. Thus the dosage of flocculant was set at 1 mg/L in this experiment. A small amount of PAC was added during filtration which could destabilize some small suspended impurities and form small flocs, and these small flocs would be conducive to the filtration process (Li & Luan 1998). The changes in turbidity, UV_{254} , and TOC of filtered water with different filter columns were measured once an hour. The filtration process was terminated and the process entered the backwashing stage under the following conditions: (1) turbidity of filtered water below the turbidity penetration value (set as 1 NTU in this experiment) and (2) the compulsory filtration cycle was less than 24 h. According to the *Water Supply and Drainage Design*

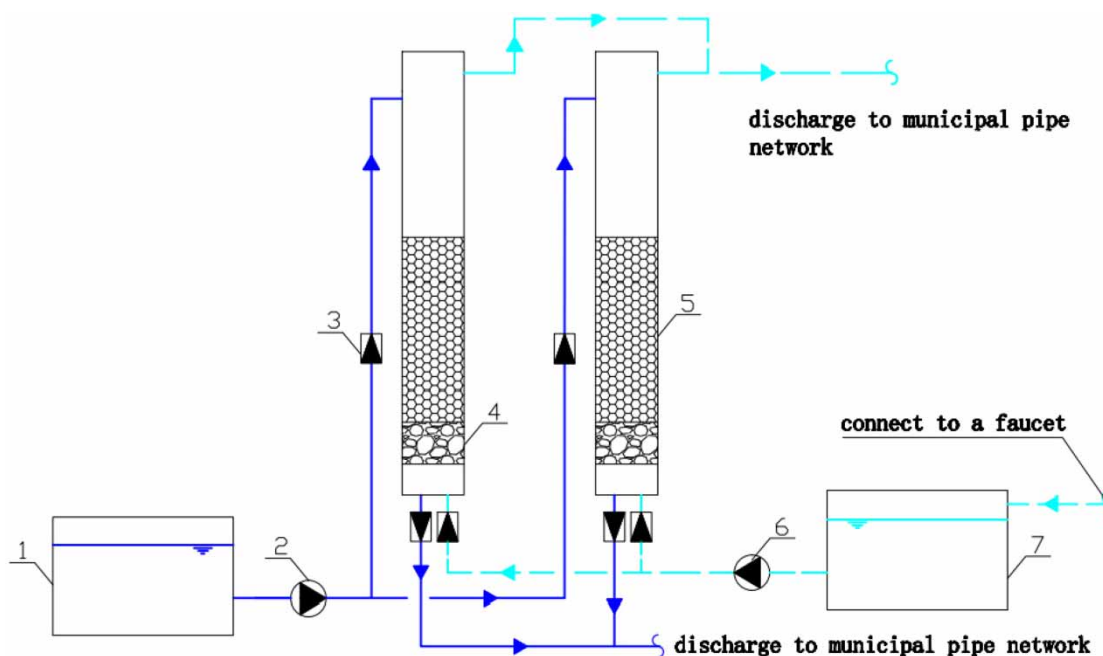


Figure 1 | Filtering experiment dynamic device diagram. 1. Raw water tank. 2. Raw water inlet water pump. 3. Flow meter. 4. Supporting layer. 5. Filtering layer. 6. Backwashing water inlet water pump. 7. Backwashing water tank.

Manual (2017), the single-layer homogeneous filter medium backwashing expansion rate should be controlled at approximately 40%, so the backwashing strength was controlled at 13 L/s·m², and the appropriate washing duration was 10 min.

2.7. Characterization methods

The determination methods in this study are all national standard methods. The water quality indicators were tested in accordance with *Water and Wastewater Monitoring and Analysis Methods (Fourth Edition)* (2002). Turbidity was measured by a Hach 2100P transmissometer (Hach, USA). The pH was measured by a pH-3C pH meter (Shanghai Precision Scientific Instrument Co., Ltd). UV₂₅₄ was measured by a UV-5500 ultraviolet spectrophotometer (Shanghai Meta-analysis Instruments Co., Ltd). TOC was measured by a TOC-2000 TOC analyzer (Shanghai Meta-analysis Instruments Co., Ltd). Filtration rate was measured by a flow meter reading algorithm. Water temperature was measured by a precision thermometer. Iron content was measured by phenanthroline spectrophotometry.

3. RESULTS AND DISCUSSION

3.1. Optimal preparation conditions of modified omphacite

3.1.1. The pH value

In this experiment, only the pH value was changed, while other preparation conditions remained unchanged. The specific preparation conditions and experimental results are shown in Table 1. While other conditions were the same, the higher the pH value, the lower the removal efficiency of organic matter. And when the pH value increased from 1 to 3, the removal efficiency decreased greatly. When the pH value increased from 3 to 11, the removal efficiency did not decrease greatly with the increase of pH. However, when the pH value increased from 11 to 13, the removal efficiency decreased significantly. This may be because when the pH is greater than 7, the isoelectric point pH₀ of the filter medium surface is less than the pH value in the solution, the hydroxide ion in the water is more attached to the oxide, so that the oxide surface is negatively charged, producing electrostatic repulsion, and the adsorption capacity is reduced. For this reason, the best pH value in this experiment was set at 1.

3.1.2. The concentration of FeCl₃

In this experiment, only the concentration of FeCl₃ was changed, while other preparation conditions remained unchanged. The specific preparation conditions and experimental results are shown in Table 2. It can be found that when the concentration of FeCl₃ increased from 1 mol/L to 2 mol/L, with the increasing of the concentration, the removal efficiency gradually increased. When the concentration of FeCl₃ was 2 mol/L, the removal effect of organic matter was the best,

Table 1 | The effect of pH on UV₂₅₄ removal efficiency

| FeCl ₃ (mol/L) | pH | Roasting temperature (°C) | Roasting time (h) | UV ₂₅₄ of influent water (cm ⁻¹) | UV ₂₅₄ of effluent water (cm ⁻¹) | Removal efficiency (%) |
|---------------------------|----|---------------------------|-------------------|---|---|------------------------|
| 2 | 1 | 550 | 2 | 0.746 | 0.325 | 56.43 |
| | 3 | | | | 0.365 | 51.01 |
| | 7 | | | | 0.374 | 48.24 |
| | 11 | | | | 0.398 | 46.64 |
| | 13 | | | | 0.421 | 43.57 |

Table 2 | The effect of modifier concentration on UV₂₅₄ removal efficiency

| FeCl ₃ (mol/L) | pH | Roasting temperature (°C) | Roasting time (h) | UV ₂₅₄ of influent water (cm ⁻¹) | UV ₂₅₄ of effluent water (cm ⁻¹) | Removal efficiency (%) |
|---------------------------|----|---------------------------|-------------------|---|---|------------------------|
| 1 | 1 | 550 | 2 | 0.792 | 0.365 | 53.91 |
| 1.5 | | | | | 0.332 | 58.08 |
| 2 | | | | | 0.313 | 60.48 |
| 2.5 | | | | | 0.358 | 54.80 |
| 3 | | | | | 0.341 | 56.94 |

indicating that the FeCl_3 at this concentration was better than the previous low concentration of the filter medium surface coverage. The removal efficiency decreased at 2.5 mol/L and 3 mol/L. It may be that the concentration of the modifier was too high, the surface porosity of the filter media was reduced, the adsorption sites were reduced, and the removal ability for organic matter decreased. Therefore, the optimal concentration of FeCl_3 is 2 mol/L.

3.1.3. Roasting temperature

In this experiment, only the roasting temperature was changed, while the other preparation conditions remained unchanged. The specific preparation conditions and experimental results are shown in Table 3. It can be seen from the table that the removal efficiency of organic matter did not illustrate a consistent change rule with the change of roasting temperature. When the roasting temperature was 450 °C, the removal efficiency of organic matter was the best. When the roasting temperature was 350 °C, the removal efficiency of organic matter was the lowest, but when the roasting temperature was 650 °C, the removal efficiency of organic matter was only higher than that at 350 °C and lower than that at 450 °C. The reason may be that when the roasting temperature is too low, the sintering strength is low, the pore structure on the oxide surface is incomplete, and the crystal morphology on the surface is not fixed, so the adsorption sites are reduced. And when the roasting temperature is too high, the crystal water and hydroxyl water inside the filter medium are lost, surface crystal morphology and spatial structure are deformed, adsorption sites are reduced, and the removal effect of organic matter decreases. In conclusion, the optimum roasting temperature is 450 °C.

3.1.4. Roasting time

In this experiment, only the roasting time was changed, while the other preparation conditions remained unchanged. The specific preparation conditions and experimental results are shown in Table 4. When the roasting time was 1 h, the removal efficiency of organic matter was the lowest, and with the increase of the roasting time, the removal efficiency of organic matter gradually increased. However, from 2 to 4 h, the removal efficiency of organic matter first increased and then decreased, the fluctuation range was not large, and the removal efficiency was close. This may be due to the fact that both the crystal state and the adsorption sites on the oxide surface reach a stable state when the roasting time is 2 h. Therefore, considering production efficiency and cost reduction, the optimal roasting time is determined to be 2 h.

3.1.5. Optimum conditions for preparation

According to the above single-factor experiments, the optimal conditions of modified preparation of the filter medium were obtained. The specific conditions and steps were as follows. The pretreated omphacite medium was weighed at approximately 100 g, immersed in a 50 ml FeCl_3 solution with a concentration of 2 mol/L, adjusted to pH = 1, stirred evenly, and then placed in an oven at 110 °C for drying. The dried omphacite medium moved to a crucible, placed in a muffle furnace for

Table 3 | Removal efficiency of UV_{254} at different roasting temperatures

| FeCl_3 (mol/L) | pH | Roasting temperature (°C) | Roasting time (h) | UV_{254} of influent water (cm^{-1}) | UV_{254} of effluent water (cm^{-1}) | Removal efficiency (%) |
|-------------------------|----|---------------------------|-------------------|--|--|------------------------|
| 2 | 1 | 350 | 2 | 0.785 | 0.323 | 58.85 |
| | | 450 | | | 0.305 | 61.14 |
| | | 550 | | | 0.321 | 59.10 |
| | | 650 | | | 0.314 | 60.0 |

Table 4 | The effect of roasting time on UV_{254} removal efficiency

| FeCl_3 (mol/L) | pH | Roasting temperature (°C) | Roasting time (h) | UV_{254} of influent water (cm^{-1}) | UV_{254} of effluent water (cm^{-1}) | Removal efficiency (%) |
|-------------------------|----|---------------------------|-------------------|--|--|------------------------|
| 2 | 1 | 450 | 1 | 0.759 | 0.322 | 57.57 |
| | | | 2 | | 0.288 | 62.05 |
| | | | 3 | | 0.286 | 62.32 |
| | | | 4 | | 0.294 | 61.26 |

roasting at 450 °C for 2 h, then taken out and cooled to room temperature. Finally, it was washed with distilled water and then dried for later use.

3.2. Surface characteristics of modified omphacite medium

3.2.1. Density and porosity

The measured data are substituted into the formulas in section 2.4, and the results are as follows:

$$\rho = \frac{G}{V_2 - V_1} = \frac{100}{125 - 100} = 4.00 \text{ g/cm}^3$$

$$m = 1 - \frac{G}{\rho V_3} = 1 - \frac{100}{4 \times 52.63} = 52.5\%$$

A comparison of the modified omphacite with the unmodified omphacite shows that the density and porosity of the modified omphacite are higher than those of the unmodified omphacite, indicating that the former can adsorb more pollutants and has a better capacity of pollution interception and turbidity removal. At the same time, with the increase in penetration depth, the increase of head loss slows down, and the water production also increases.

3.2.2. Specific surface area

Table 5 illustrates the BET test results. The results reveal that the specific surface area of modified omphacite is 4.65 times that of the unmodified omphacite. This finding also shows that the adsorption capacity of the modified filter medium is greatly increased.

3.2.3. Scanning electron microscopy

Figure 2 is the SEM photograph of the surface of the omphacite before and after modification. The surface of the unmodified filter medium is relatively smooth, with fewer prominent ravines, so its porosity, specific surface area and adsorption capacity are small. The modified omphacite filter medium electron microscopy shows that it has many surface particles. Although covered in iron oxide, the surface has many grooves, resulting in its surface area being higher than the unmodified omphacite. This finding proves that the porosity of modified omphacite is higher and the modifier bearing capacity is higher and more uniform.

Table 5 | Specific area of filter medium

| Filter medium | Sampling quality (g) | Total surface area (m ²) | Specific surface area (m ² /g) |
|--------------------|----------------------|--------------------------------------|---|
| Omphacite | 5.15 | 1.49 | 0.29 |
| Modified omphacite | 5.37 | 7.25 | 1.35 |

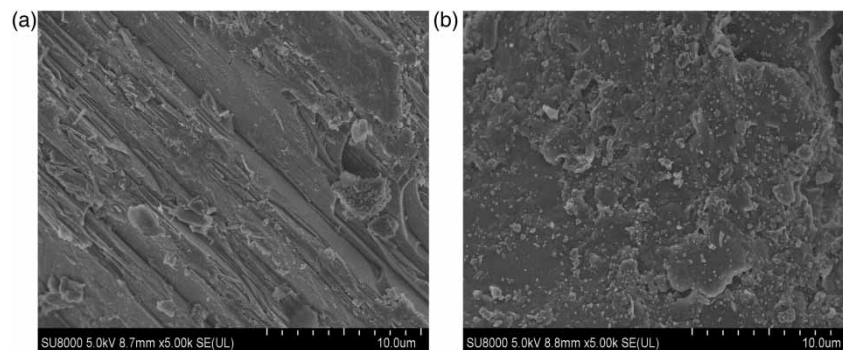


Figure 2 | SEM photograph of omphacite filter medium and modified omphacite filter media ($\times 5000$): (a) omphacite filter media; (b) modified omphacite filter media.

3.2.4. Spectrum analysis

Figure 3 shows the detection position of EDS in the unmodified and modified omphacite, and Figures 4 and 5 show the energy spectrum analysis of these two filter media. The point-EDS energy spectrum analyses of the unmodified omphacite shows that the content of Fe, Mg, and Si varies greatly at different points, indicating that the element mass percentage of the surface layer and fractured surface of the unmodified omphacite is different. The point-EDS energy spectrum analyses of the modified omphacite shows that the difference in the mass fraction of Fe elements at different points is reduced compared with that before modification. These findings all express that the iron content of the modified omphacite filter medium is increased and the iron coverage on the surface is uniform.

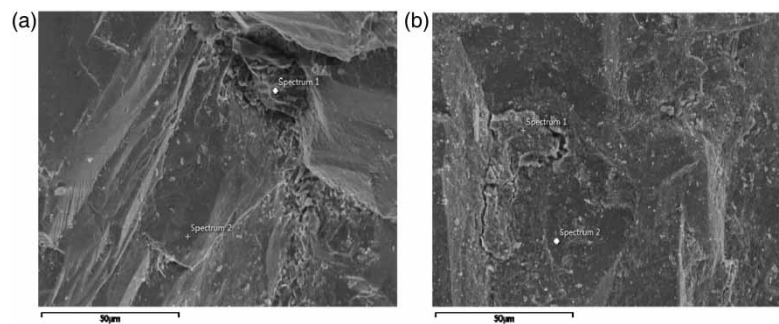


Figure 3 | Position of the omphacite rough EDS and the modified omphacite EDS: (a) position of the omphacite EDS; (b) position of the modified omphacite EDS.

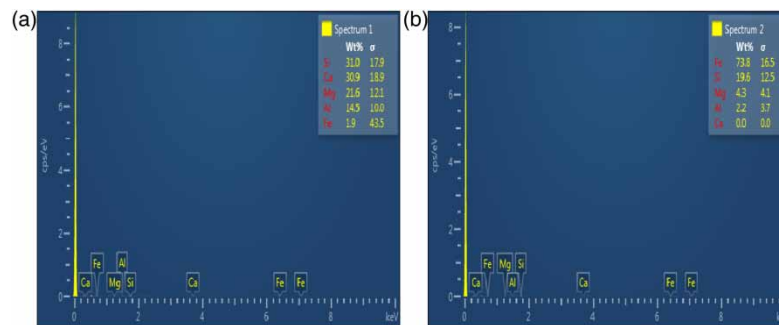


Figure 4 | Different point-EDS energy spectrum analyses of the omphacite: (a) point I EDS energy spectrum; (b) point II EDS energy spectrum.

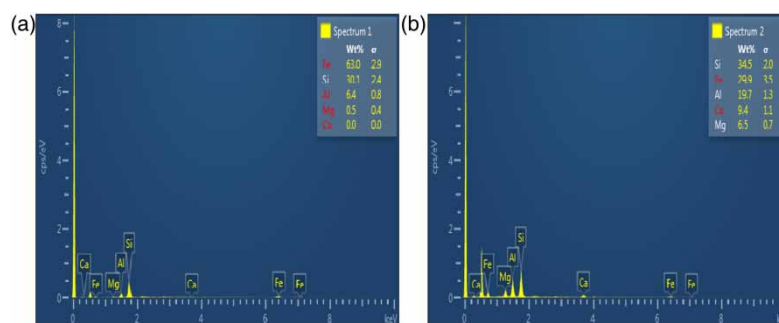


Figure 5 | Different point-EDS energy spectrum analyses of the modified omphacite: (a) point I EDS energy spectrum; (b) point II EDS energy spectrum.

Table 6 | Anti-interference effect of modified filter medium

| Interference factor | Original iron coated UV ₅₁₀ (cm ⁻¹) | Iron coated after interference UV ₅₁₀ (cm ⁻¹) | Loss efficiency (%) |
|------------------------|--|--|---------------------|
| High flushing strength | 0.128 | 0.1271 | 0.70 |
| pH = 3 | 0.128 | 0.1265 | 1.17 |
| pH = 12 | 0.128 | 0.1262 | 1.5 |

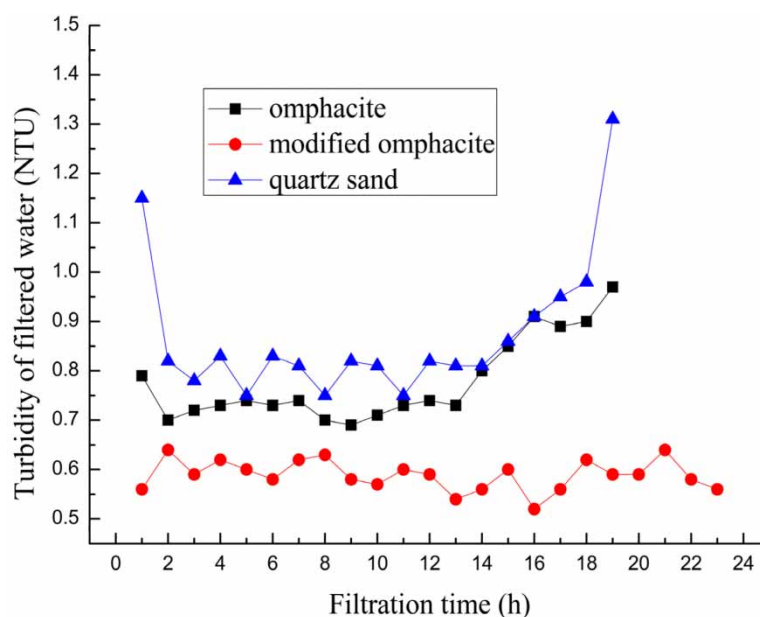
3.3. Study on the stability of modified omphacite filter

The anti-interference research results of the modified filter medium under different conditions is presented in Table 6. As revealed in the table, the modified omphacite has strong impact resistance, and the losses of iron coating are low in high-intensity washing and in acidic and alkaline environments, all of which are less than 1.5%.

3.4. Dynamic adsorption experiment of filtration medium

3.4.1. Removal of turbidity

The comparison of the turbidity removal effect between quartz sand, unmodified omphacite, and modified omphacite filter medium is depicted in Figure 6. In the filtration cycle, the average effluent turbidity of the quartz sand, unmodified omphacite, and modified omphacite filter columns were 0.86, 0.76, and 0.58 NTU, respectively. Compared with the turbidity of the influent water (15.75 ± 4.12 NTU), the average removal efficiency of turbidity of quartz sand, unmodified omphacite and modified omphacite were 94.5%, 95.2%, and 96.3%, respectively. Thus, the modified omphacite filter column had the best turbidity removal effect among the three filter columns. Compared with the other two filter columns, the turbidity fluctuation of the quartz sand filter column was larger, indicating that the removal ability of the quartz sand filter layer was uneven. The modified omphacite filter column was stable with low effluent. The maximum effluent turbidity was 0.64 NTU, the minimum turbidity was 0.52 NTU, and the fluctuation range was small. Within the limited filtration cycle, the effluent of the modified omphacite filter column can remain below 1 NTU at 24 h, whereas the filtration cycle of the unmodified omphacite filter column is only 19 h. In the later filtration period, the water quality deteriorated and the effluent water quality fluctuated greatly. Combined with electron microscope and energy spectrum analysis, the possible reason for this finding is that compared with the unmodified omphacite, the surface of the modified omphacite is rougher, the specific surface area is larger, the porosity is higher, and the pollution interception and turbidity removal ability are stronger. The isoelectric point of the

**Figure 6** | Curves of turbidity removal by three filter medium with time.

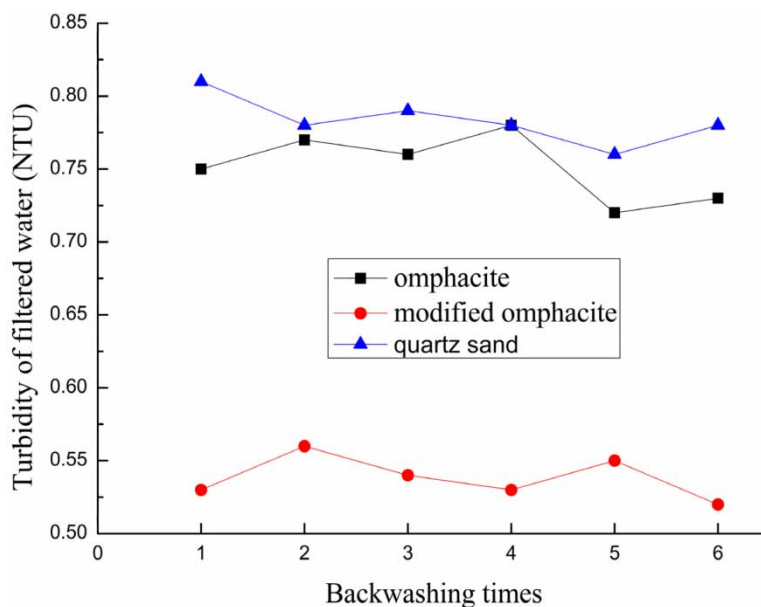


Figure 7 | Relationship between turbidity of effluent and backwash times.

modified omphacite increased and the adsorption force between the modified omphacite and negatively charged suspended particles in the water was enhanced, thereby the effect of turbidity removal further improved.

Figure 7 shows that different backwashing times have little influence on the turbidity removal effect of the quartz sand, unmodified omphacite, and modified omphacite filter column. And the removal effects of the three filter columns are relatively stable. In each filtration cycle, the average turbidity after filtration of the quartz sand, unmodified omphacite, and modified omphacite filter column was maintained at 0.76–0.81 NTU, 0.72–0.78 NTU, and 0.52–0.56 NTU, respectively. A possible reason for this finding is that the removal of turbidity in raw water mainly depends on the physical retention of the filter medium. Although the adsorption of turbidity by the modified filter medium decreases to a certain extent with the increase of filtration times, it has little influence on the overall filtration performance of the filter column. Therefore, the interception effect of the filter medium on suspended solids can be restored by the combined action of shear force and collision force when high-speed water backwash is used.

3.4.2. Removal of UV₂₅₄ and TOC

The comparison of the organic matter removal effect in the quartz sand, unmodified omphacite, and modified omphacite filter columns is presented in Figure 8. In terms of organic matter removal efficiency, the modified omphacite reveals a considerable improvement over the unmodified omphacite. The average organic matter removal efficiency of the modified omphacite was 50.35% in the filtration cycle, higher than the 23.46% of the unmodified omphacite and 21.17% of the quartz sand. A possible reason for this phenomenon is that organic pollutants, carboxyl, alcohol hydroxyl, phenol hydroxyl, and other negatively charged functional groups were more numerous in the water. And the surface of unmodified omphacite also has a negative charge. Owing to the existence of electrostatic repulsion, the surface of the unmodified filter medium cannot easily attract organic pollutants, making the removal efficiency of organic matter very low and the removal effect of organic matter through physical action very small. By modifying, the surface of the modified omphacite is covered with positively charged iron oxides, and iron oxides in the filtration process will first contact water molecules and hydroxyl, resulting in ion exchange with anion functional groups of organic matter, thereby removing the organic matter.

Figure 9 shows the changes of TOC removal effect in each filter column. As can be seen from the figure, the TOC removal efficiency of quartz sand is very low, at only approximately 2.2%, potentially because the surface of quartz sand is smooth, thereby the adsorption capacity of small molecular organics is weak. Compared with the average removal efficiency of 26.7% by unmodified omphacite for TOC, the average removal efficiency by modified omphacite reaches 45.5%, representing a considerable improvement. The results reveal that the adsorption capacity of omphacite on organic compounds containing hydrophilic hydroxyl, carboxyl, and aldehyde groups in water was greatly improved after

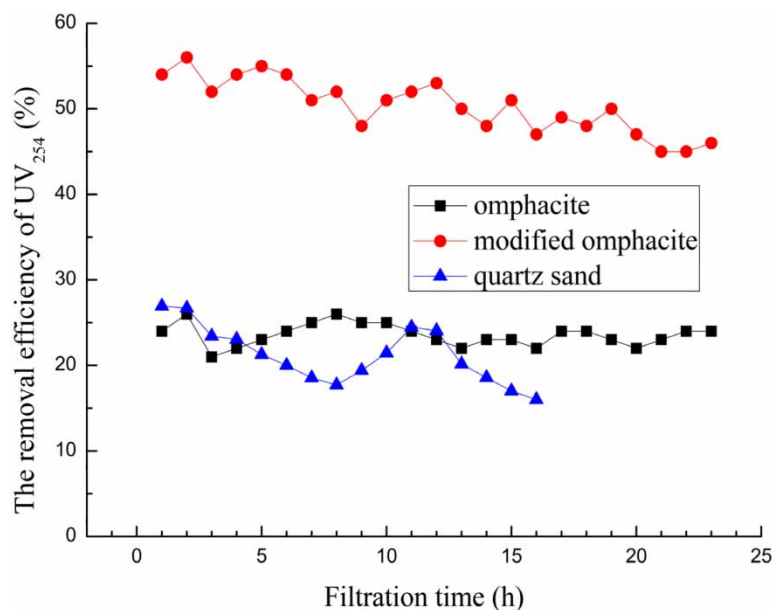


Figure 8 | Curves of UV₂₅₄ removal efficiency by three filter media with time.

modification. A possible reason for this finding is that the surface of the modified filter medium is covered with positively charged iron oxide, which can more easily react with these functional groups, thereby achieving the removal of hydrophilic small molecular organic matter.

During the filtration period, the UV₂₅₄ of the influent water was 0.350 cm⁻¹, and the backwashing method of clear water was adopted. The UV₂₅₄ value of the average filtered water within the filtration period was taken as the reference index in the experiment, as revealed in Figure 10. After six iterations of backwashing with clear water, the quartz sand, unmodified omphacite, and modified omphacite filter columns indicated a certain stability in the removal effect of organic matter. The reason for this phenomenon is the physical interception to achieve the removal of organic matter, so the intercepted

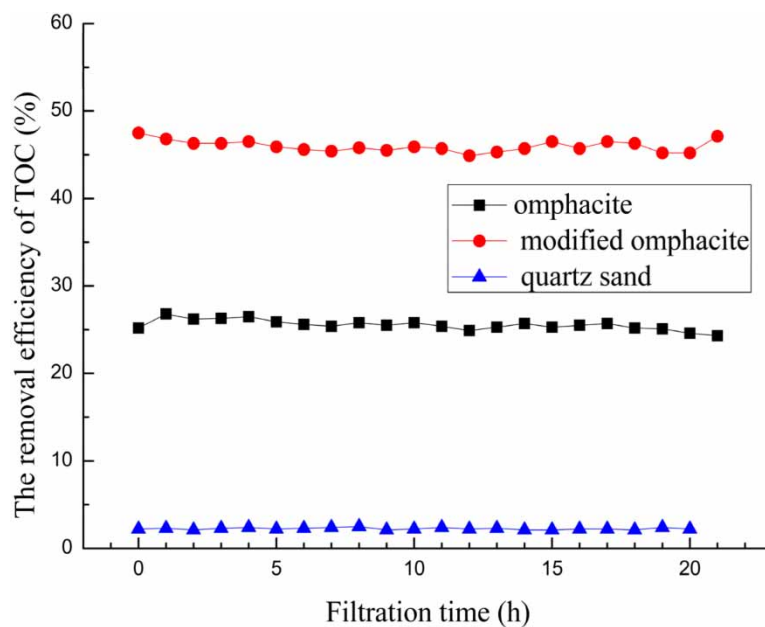


Figure 9 | Curves of TOC removal efficiency by three filter media with time.

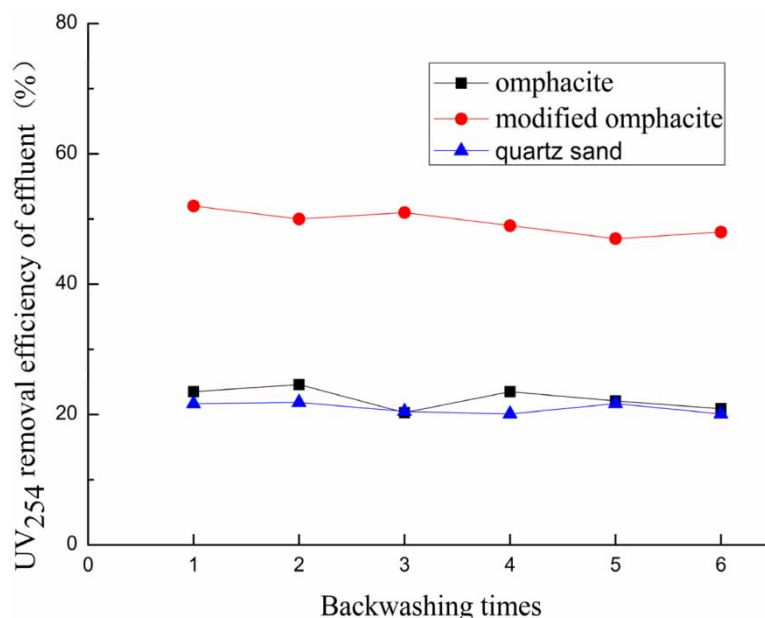


Figure 10 | Relationship between UV_{254} of effluent and backwash times.

of organic matter is often left on the surface of the filter medium. Relying on the water backwash shear force and collision force can restore its organic matter removal performance. However, the removal of organic matter by the modified omphacite filter column includes chemical adsorption, electrostatic adsorption, and physical interception. The adsorbed organic matter is often closely attached to the inner layer of the filter medium. Recovering its removal performance of organic matter by the shear force and collision force of backwash of water flow alone is difficult.

4. CONCLUSIONS

In this experiment, $FeCl_3$ was used as a modifier to prepare a modified omphacite filter medium by roasting at high temperature. The optimal preparation conditions are as follows: the pH value is 1, concentration of $FeCl_3$ is 2 mol/L, roasting temperature is 450 °C and roasting time is 2 h.

The specific surface area of the modified omphacite filter medium is increased from 3.35 g/cm³ to 4 g/cm³ and the porosity is increased from 49.5% to 52.5%. Scanning electron microscopy, specific surface area and energy spectrum analysis revealed that the surface structure of the modified omphacite filter medium changes greatly, the surface is rougher and potholes increase. Thus the specific surface area and adsorption capacity increase significantly.

The dynamic filtration and backwashing experiment of the three filter medium revealed that the average removal efficiency of organic matter by modified omphacite reached 50.35%, which was higher than the 23.46% by the unmodified omphacite and 21.17% by quartz sand. The average removal efficiency of TOC by modified omphacite was 45.5%, which was higher than the 26.7% by unmodified omphacite and 2.2% by quartz sand. The average removal efficiency of turbidity by modified omphacite was 96.3%, which was higher than the 95.2% by unmodified omphacite and 94.5% by quartz sand. After modification, the removal ability for organics was obviously improved, and the backwashing performance was effectively recovered. In general, the modified omphacite has certain advantages in turbidity removal, organic matter removal, and backwashing recovery ability, so the modified omphacite should be further investigated to reveal its practical application effects in engineering.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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