

Filtration characteristics of garnet media before and after modification

Wu Huifang, Yue Lingzhi, Wang Zhiyuan, He Jiang, Chen Ruoya and Li Xiang

ABSTRACT

High-temperature calcination was used to modify garnet media. Brunauer–Emmett–Teller (BET) measurements, X-ray diffractometer (XRD), scanning electron microscopy (SEM), zeta potential analysis, and a static adsorption experiment on humic acid removal were carried out to compare unmodified garnet and traditional quartz sand. Fitting adsorption isotherm of the media before and after modification was conducted to determine the adsorption type, and a dynamic filtration experiment was performed to treat micro-polluted water. Results of the characterization analysis and the static adsorption experiment revealed that, compared with the smooth surface of unmodified garnet, the surface of modified garnet media was covered with Fe_2O_3 , which showed a rough concave-convex structure with a specific area that was 2.44 times larger than that of unmodified garnet. The removal efficiency of organic matter after modification increased from 2.5–4.5% to 51.7–63.1%, and the adsorption capacity increased 11–24 times. The adsorption type of the modified garnet media belongs to the Langmuir and Freundlich adsorption mode, while that of the original media belongs to the Freundlich adsorption mode. Results of the dynamic filtration experiment revealed that the effect of modified garnet media on turbidity, COD_{Mn} , and UV_{254} removal was better than that of unmodified garnet and traditional quartz sand.

Key words | adsorption capacity, adsorption isotherm, dynamic filtration, humic acid, modified garnet media

Wu Huifang (corresponding author)
Yue Lingzhi
Wang Zhiyuan
He Jiang
Chen Ruoya
Li Xiang
Department of Municipal Engineering,
College of Urban Construction,
Nanjing Tech University,
Nanjing 211816, Jiangsu,
China
E-mail: h.f.wu@163.com

INTRODUCTION

China is one of the 12 poorest countries in the world in terms of per capita water resources (Li 2014), while the people's demand for a high-quality, healthy life is increasing. Therefore, water pollution will certainly become a major obstacle in China's sustainable development. There are considerable resources of natural organic matters (NOM) in the water environment. The content of humus accounts for 50–90% of NOM (Liu *et al.* 2017), and humic acid is the main component of humus. The presence of humic acid will enhance the

solubility of micro-pollutants in water, produce a variety of carcinogenic disinfection by-products during the disinfection process, and reduce the photodegradation efficiency of microcystins (Imai *et al.* 2009). In the newly issued drinking water quality standards in China, among the newly added indicators, toxicology indicators account for 59 items, organic compounds account for 70%, and the majority are small organic molecules (Standards for drinking water quality-GB5749-2006). It shows that the Chinese people are paying more and more attention to micro-polluting organic matter.

Most domestic water plants currently adopt the traditional water treatment process of 'coagulation/precipitation/filtration/disinfection'. Filtration is the core water purification unit of the water treatment process.

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

doi: 10.2166/wrd.2020.070

The filtration performance of the filtration material has a direct impact on the effluent quality of the filter chamber (Elbana *et al.* 2012). Granular filtration materials such as quartz sand are commonly used as filtration media in the sand filter. However, the removal ability of ordinary granular filtration materials on negatively charged organic matter and small particle pollutants is limited (Wang *et al.* 2010; Huang *et al.* 2012; Zarchi *et al.* 2013) because of their small specific surface area, small adsorption capacity, low isoelectric point, and low porosity (Li *et al.* 2016; Verma *et al.* 2017). Therefore, studying new natural filtration materials and changing the properties of filtration materials through artificial methods are crucial to improving the removal efficiency of pollutants. For this reason, domestic and foreign researchers have used metal oxides as modifiers on the surface of traditional filtration materials (e.g., quartz sand and ceramsite) to carry out modification experiments (Yadav *et al.* 2013) via high-temperature calcination and repeated deposition (Boujelben *et al.* 2009). Commonly used modifiers include aluminum, iron oxides, hydroxides, and magnesium oxides, among which iron oxides and aluminum oxides are the most widely used (Eisazadeh *et al.* 2013). Domestic and foreign research on the filtration and adsorption capacity of modified filtration materials demonstrate these filtration materials have obvious removal effects on common pollutants, such as turbidity and organic matter in water. Li *et al.* (2012) carried out filtration and backwash experiments and found that the effect of quartz sand media modified by iron oxide on pollutant removal, especially on organic matter removal, is greatly improved. Zhao *et al.* (2007a) compared the adsorption effects of modified quartz sand media, modified ceramsite media, original quartz sand media, and original ceramsite media on organic matter. They found that the modified filtration material has considerably better adsorption and removal effect on the organic matter than the original filtration material. Iron-coated quartz sand has the best effect on the removal of organic matter among these various media. Boujelben *et al.* (2009) prepared natural iron oxide-coated modified quartz sand (NCS) and studied its adsorption and removal performance for Cu and Ni under the influence of stirring time, pH value, initial metal ion concentration, and temperature. The results showed that NCS had better adsorption and removal performance for Cu and Ni. Ding *et al.* (2010) used

cetyltrimethylammonium (HDTMA) to modify iron oxide sand (IOCS) and measured its adsorption and removal performance as a sorbent for NOM in water. The test results showed that HDTMA-modified IOCS had a faster initial adsorption of NOM and its adsorption capacity in the filter column was higher than that of unmodified IOCS.

The application of modified filtration materials is very extensive. The efficiency of them on removing some pollutants has been recognized by many scholars. In order to make better-modified filtration materials, it is necessary to find better carrier filtration materials. The East China Sea area of Lianyungang (in Jiangsu Province) has abundant mineral resources. However, garnet tailings produced in the process of mineral exploitation cannot be utilized. Large-scale tailings hoarding has become an important factor restricting the sustainable development of mines and endangering the ecological environment of mining areas and surrounding areas. Comprehensive utilization of tailings has become an inevitable choice for economic development and environmental protection (Liciskó *et al.* 1999; Matschullat *et al.* 2000). Garnet tailings were selected as filtration materials to realize the recycling of resources. At the same time, as a water treatment material, garnet has excellent characteristics in filtration. Firstly, compared with traditional quartz sand media, garnet media has a higher specific surface area and can be loaded with more modifiers during modification. The crystal structure of traditional quartz sand media and other filtration materials is circular or elliptical, while the garnet media has a polyhedral crystal structure which improves the porosity between the filter layers and adsorption capacity. Secondly, the Mohs hardness of garnet media reaches 7.0–8.0, while that of traditional quartz sand media is 4.5–6.0. So the breakage of garnet media is low and the service life is long. In addition, the porosity of traditional quartz sand media is usually 38–42%, while that of garnet media is usually 48–53% which enhances the removal effect of pollutants (Dong & Xu 2017). Previously, we have carried out experiments to prove that the removal effect of garnet media on pollutants is significantly better than the traditional quartz sand media (Wang *et al.* 2018). However, similar to traditional quartz sand media, it has limitations in the removal of organic matter.

In the present study, modified garnet media was prepared via high-temperature calcination with ferric chloride as a

modifier. The high specific surface area of raw garnet media can load more iron oxides than that of traditional quartz sand media. The adsorption and removal effects of modified garnet media on the organic matter were studied through a static adsorption experiment. The adsorption mode was studied and compared with those of unmodified garnet media and traditional quartz sand media. Simultaneously, the filtration performance of modified garnet media on micro-polluted water was further studied by a dynamic filtration experiment. This study aims to improve the treatment effect of micro-polluted water and broaden the application of modified garnet media as water treatment filtration material.

MATERIALS AND METHODS

Materials

Garnet was obtained from a mineral company in Jiangsu; quartz sand was collected from a water plant in Jiangsu; humic acid and phenanthroline were purchased from Aladdin Reagent Co., Ltd (Shanghai, China); concentrated hydrochloric acid and sodium hydroxide were purchased from Nanjing Chemical Reagent Co., Ltd (Nanjing, China); potassium manganate and polyaluminum chloride (PAC) were purchased from Sinopharm Chemical Reagent Co., Ltd (Nanjing, China); and ferric chloride was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China).

Filtration material

Garnet, black, particle size $\Phi = 0.5\text{--}1.2$ mm, $d_{10} = 0.56$ mm, specific surface area $S = 0.32 \times 10^4$ cm²/g, porosity $e = 51\%$; quartz sand, yellow, particle size $\Phi = 0.5\text{--}1.2$ mm, $d_{10} = 0.60$ mm, specific surface area $S = 0.15 \times 10^4$ cm²/g, porosity $e = 41\%$.

Preparation of modified garnet media

The surface of the garnet media was pretreated to restore its surface properties. The specific pretreatment method was as follows. Garnet media with a particle size range of 0.5–1.2 mm was sieved using a standard sieve. After rinsing, the media was immersed in 0.1 mol/l hydrochloric acid solution for 24 h and then washed and placed in an oven for

drying. Finally, the garnet media was cooled to room temperature for use. After pretreatment, it was modified via high-temperature calcination. The specific calcination method was as follows. Garnet media with an approximate volume of 50 ml (bulk density = 2.2 g/cm³, mass range = 110 ± 2.132 g) was weighed and immersed in a 50 ml FeCl₃ solution with a concentration of 2 mol/l. It was then dried in an oven to constant weight while mixing once an hour to prevent media bonding. The garnet media was calcined in a muffle furnace at 450 °C for 2 h and then taken out and cooled to room temperature in a crucible. Finally, it was washed with distilled water and then dried for use.

Surface characteristics of modified garnet media

The specific surface areas of the garnet media before and after modification were measured via the Brunauer–Emmett–Teller (BET) specific surface area method (BET, 3H-2000PS1, China). Surface compositions of the garnet media before and after modification were identified by XRD (Rigaku, Japan). Surface conditions of the garnet media before and after modification were analyzed by scanning electron microscopy (SEM, JSM-6510, USA; EDS, NS7, USA). The charges on the surface of garnet before and after modification were measured by zeta potential (Zetasizer, Nano ZS, UK).

Study on the stability of modified garnet media

The stability of the modified media was measured under high flushing strength and an acid–base environment. It was evaluated through the shedding of the iron on the media surface. (1) In the test for measuring physical stability, 100 g modified garnet media was weighed and placed in a plexiglas filter column with an inner diameter of 20 mm and a height of 1.2 m. The media was rinsed continuously for 24 h at a high wash intensity of 12 l/s·m². The change in iron content before and after rinsing was measured using the phenanthroline method. (2) In the test for measuring chemical stability, double 1 g modified garnet media were weighed and immersed in 100 ml hydrochloric acid solution of pH = 3 and 100 ml sodium hydroxide solution of pH = 12, respectively. After the media was shaken at a speed of 180 r/min in a shaker for 24 h, it was taken out, and then the change in iron content on the media surface before and after the reaction was

measured using the phenanthroline method. Additionally, surface conditions of the modified garnet media before and after backwashing were identified by SEM-EDS and XRD.

Static adsorption experiment

Batch equilibrium method was used in the adsorption experiment. The appropriate amount of humic acid was weighed, diluted with distilled water, and then shaken up. Next, 100 ml organic raw water with respective concentrations of 4.82, 10.63, 20.25, 29.86, and 39.62 mg/l were prepared in a beaker, and their pH was adjusted to neutral. Equal volumes of modified garnet media, unmodified garnet media, and quartz sand media (bulk density and mass range of quartz sand was 1.6 g/cm^3 , $80 \pm 1.654 \text{ g}$, respectively) were added in the organic raw water. These were then placed in an oscillator at a speed of 100 r/min for 3 h and then left to stand for 40 min. The changes of UV_{254} in the supernatant before and after the oscillation were measured and the changes in the organic concentration were obtained.

Dynamic filtration experiment

Figure 1 illustrates the experiment device used in this research. The plexiglas filter column has a diameter of 30 mm and a height of 1,500 mm. A pebble-supporting layer with a thickness of 100 mm was placed on the bottom of

the filter layer. The experimental influent water was taken from the micro-polluted water in the campus lake. The average influent water quality and fluctuation range during the experiment were as follows: turbidity: $16.32 \pm 5.80 \text{ NTU}$, COD_{Mn} : $8.32 \pm 1.10 \text{ mg/l}$, UV_{254} : $0.116 \pm 0.032 \text{ cm}^{-1}$.

The modified garnet media, unmodified garnet media, and quartz sand media with a thickness of 800 mm were packed in different filter columns. The filtration method was micro-flocculation filtration with a constant filtration rate of 8 m/h. The empty bed residence time was 6 min. PAC was selected as the flocculant at a dosage of 1 mg/l. The changes in turbidity, COD_{Mn} , and UV_{254} of the filtered water in different filter columns were measured once an hour. Filtration was terminated and the process entered the backwashing stage (using a water-washing method while adding 0.05 mol/l sodium hydroxide as an assistant) when the following cases occurred. (1) The turbidity of the filtered water continued to increase until it reached the turbidity penetration value (this experiment was set as 1 NTU). (2) The compulsory filtration cycle was less than 24 h.

Analysis method

The determination methods in this study were all national standard methods. The testing of various water quality indicators was carried out in accordance with the Water and Wastewater Monitoring and Analysis Method (4th edn).

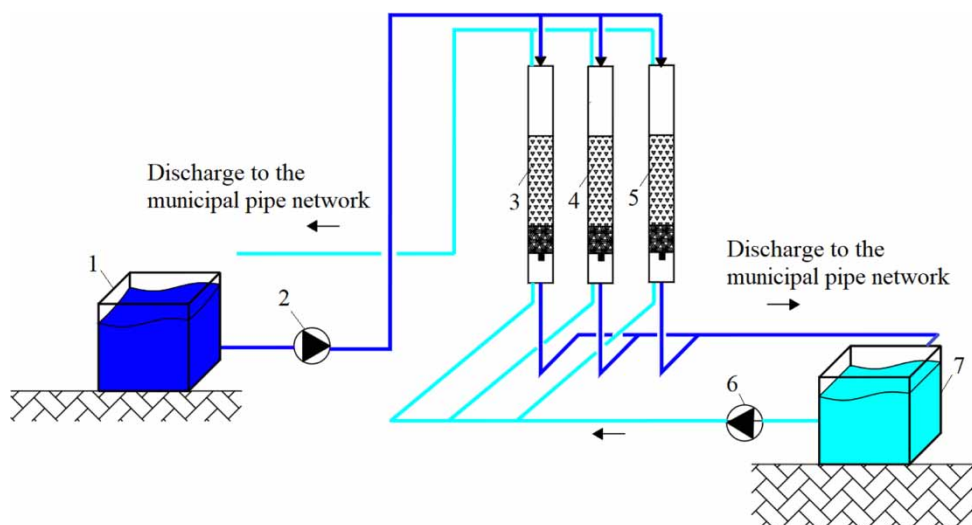


Figure 1 | Diagram of the dynamic filtration experiment device. 1 – Raw water tank; 2 – peristaltic pump; 3 – modified garnet filter column; 4 – garnet filter column; 5 – quartz sand filter column; 6 – circulation pump; 7 – backwash water tank.

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). UV_{254} was measured by a UV-5500 ultraviolet spectrophotometer (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. Chemical oxygen demand (COD_{Mn}) was measured by the acidic potassium permanganate method.

RESULTS AND DISCUSSION

Surface characteristics of modified garnet filter

Specific surface area

The BET results indicated that the specific surface areas of the unmodified garnet media and the modified garnet media were 0.32 and 0.78 m^2/g , respectively. The specific surface area of the modified garnet media was 2.44 times that of the unmodified garnet media.

X-ray diffraction

The XRD results of the unmodified and modified garnet media are depicted respectively in Figure 2. Compared with the standard map, the characteristic peaks of the unmodified garnet media mainly coincided with FeO, SiO_2 , and Al_2O_3 . The peak value of the modified garnet media

basically coincided with Fe_2O_3 , and the peak intensity was high. The result indicated that the material attached to the surface of the modified garnet media was basically Fe_2O_3 . Simultaneously, the peaks of FeO, SiO_2 , and Al_2O_3 were less, which indicated that Fe_2O_3 substantially covered the surface of the garnet media.

Scanning electron microscopy

The SEM photograph of the surface of the garnet media before and after modification is shown in Figure 3. The surface of the unmodified garnet media was smooth and flat with a few small pits and pores. The specific surface area and adsorption capacity were small. By contrast, the surface structure of the modified garnet media was completely different; it was rougher with many snowflake-shaped pits. Therefore, the specific surface area and adsorption capacity of the modified garnet media were increased. It can be seen from the EDS result that most components of the surface of the modified garnet media were Fe_2O_3 with a few of SiO_2 and FeO. This result was consistent with the XRD result of the modified garnet media.

Zeta potential

The zeta potential of the surface of the garnet media before and after modification is shown in Figure 4. The isoelectric point (pH_0) of the garnet before modification is between 3 and 4 and that of the modified garnet is between 7 and 8. In the micro-polluted water with neutral pH, the surface of the garnet media before modification is negatively charged, while the surface of the modified garnet media is positively charged.

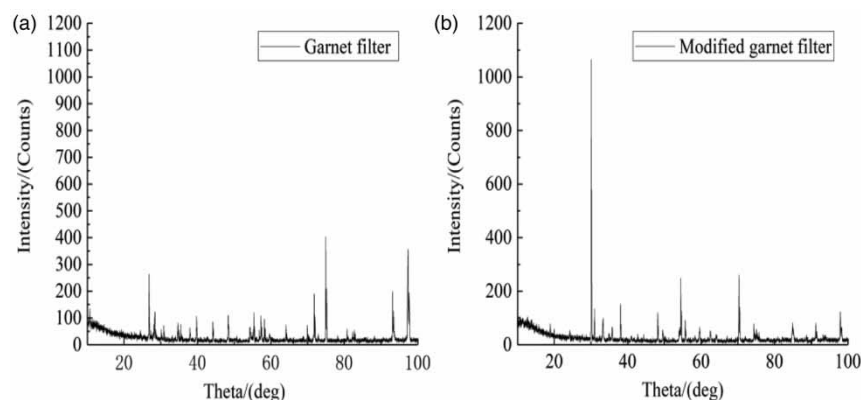


Figure 2 | XRD results of the garnet media before and after modification. (a) Garnet media. (b) Modified garnet media.

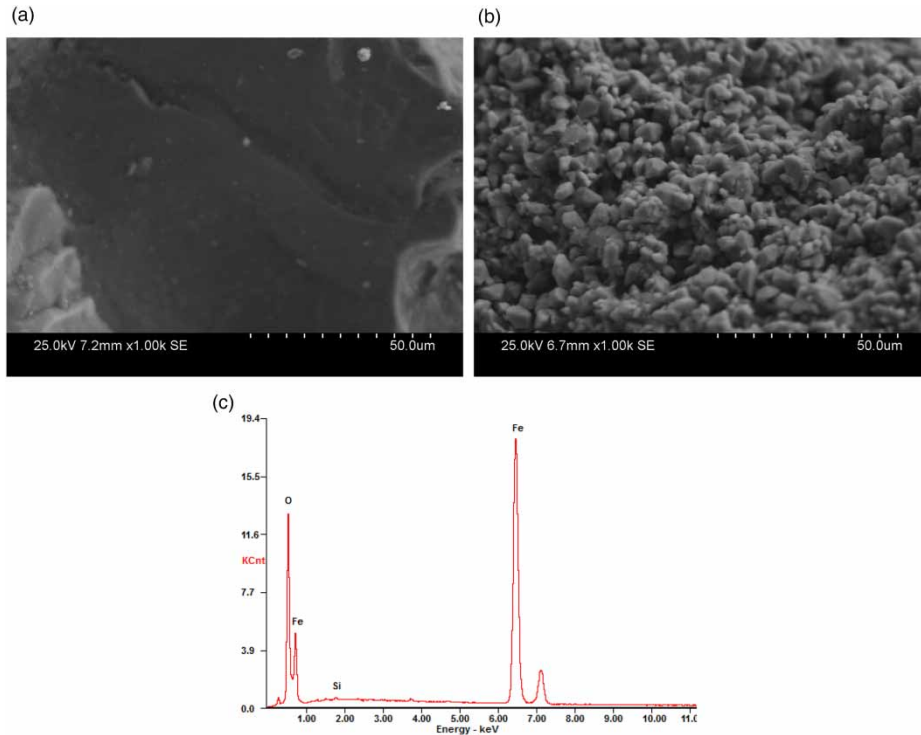


Figure 3 | SEM photographs of the surface of the garnet media before and after modification ($\times 1,000$). (a) Garnet media. (b) Modified garnet media. (c) Modified garnet media.

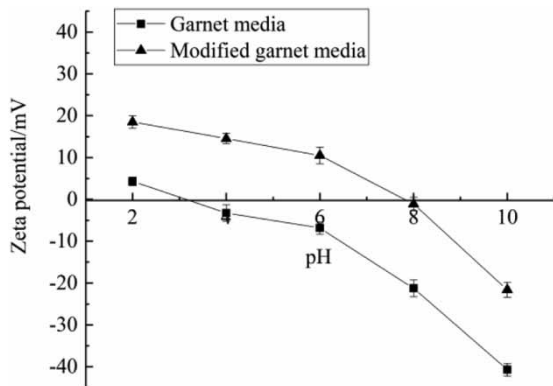


Figure 4 | The zeta potential of the surface of the garnet media before and after modification.

Study on the stability of modified garnet filter

The stability of the modified garnet media was measured under high flushing strength and an acid–base environment. It was evaluated through the shedding of the iron on the surface of the modified media. The experimental results are presented in Table 1, revealing that the modified garnet media has good physical strength and chemical stability. Its loss rate was less than 1% in high flushing strength and

Table 1 | Results of the stability experiment of modified garnet media

Interference factor	Original iron coated (UV_{510}) (cm^{-1})	Iron coated after interference (UV_{510}) (cm^{-1})	Loss rate (%)
High flushing strength	0.979	0.974	0.51
pH = 3	0.979	0.973	0.61
pH = 12	0.979	0.970	0.92

an acid–base environment. This finding indicates that the modifier was stably attached to the surface of the garnet media to adsorb organic matter better.

At the same time, the surface of the modified garnet media before and after backwashing was tested by SEM-EDS and XRD. SEM photographs and XRD results of the surface of the modified garnet media before and after backwashing are shown in Figures 5 and 6, respectively. It can be seen from SEM images that the surface of the modified garnet media was covered with a layer of contaminants before backwashing. The contaminants were basically removed after backwashing while a very small amount of modifier was detached. It can be seen from the EDS results that most

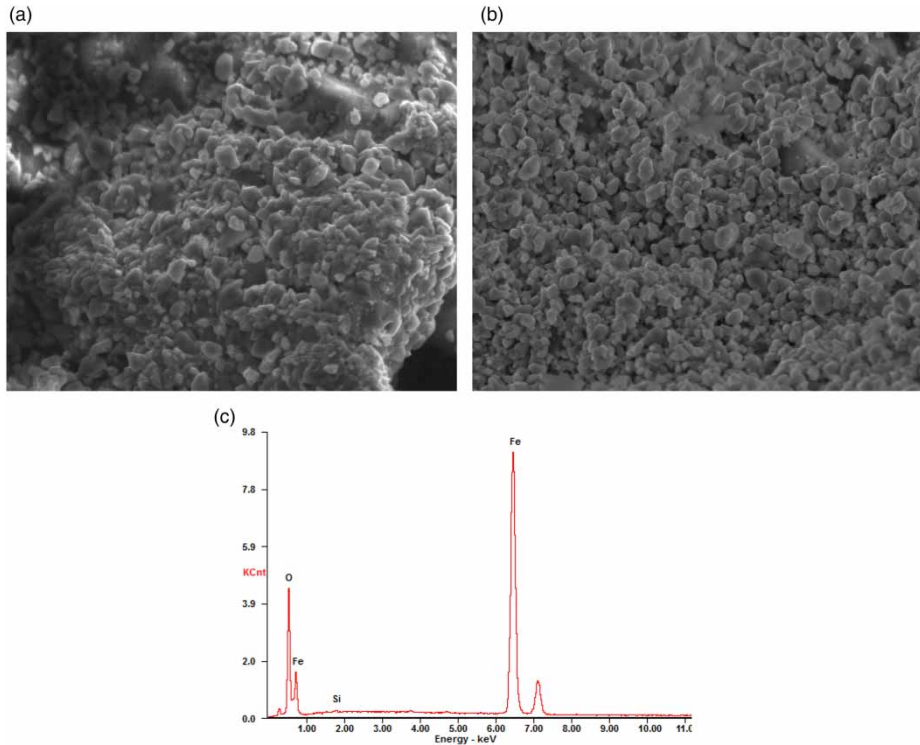


Figure 5 | SEM photographs of the surface of the modified garnet media before and after backwashing ($\times 1,000$). (a) Modified garnet media before backwashing. (b) Modified garnet media after backwashing. (c) Modified garnet media after backwashing.

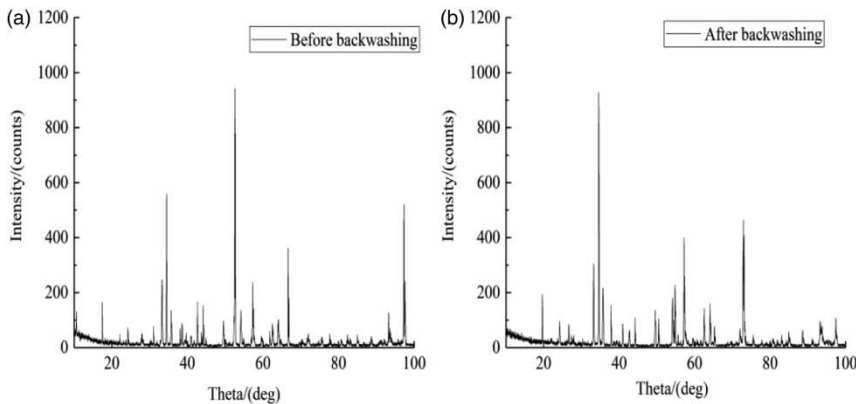


Figure 6 | XRD results of the surface of the modified garnet media before and after backwashing. (a) Modified garnet media before backwashing. (b) Modified garnet media after backwashing.

components of the surface of the modified garnet media after backwashing were still Fe_2O_3 , indicating that the modifier was stably attached to the surface of the garnet. It can be seen from the XRD results that the peak of Fe_2O_3 on the surface of the modified garnet media before backwashing was weak due to a layer of contaminants and a new peak appeared at the same time. The peak of Fe_2O_3 became stronger after

backwashing. However, compared with the Fe_2O_3 peak on the surface of the modified garnet media in Figure 2(b), that of the modified garnet media after backwashing was slightly lower and the peaks of FeO , SiO_2 , and Al_2O_3 were slightly higher, indicating that a small amount of modifier was detached. In summary, most modifiers were still attached to the garnet surface after backwashing.

Static adsorption experiment of filtration media

Adsorption effect

The adsorption effects of the quartz sand media, unmodified garnet media, and modified garnet media on organic matter after adsorption equilibrium under different concentrations of organic raw water (4.82, 10.63, 20.25, 29.86, and 39.62 mg/l) are depicted in Tables 2 and 3.

Table 2 reveals that under the same concentration of humic acid, the removal rate of organic matter by modified garnet media (51.87–63.13%) was significantly higher than that of unmodified garnet media and quartz sand media. At the same time, the removal rate of organic matter by unmodified garnet media (2.55–4.56%) was slightly higher than that of quartz sand media (2.44–4.56%). Probably because the surface of garnet and quartz sand media before modification is smooth, the organic matter is only physically adsorbed by the specific surface area and pores of filtration materials. As can be observed from Figure 3, the surface roughness and specific surface area of the modified garnet media are increased, which can thereby increase the active adsorption sites and improve the physical adsorption effect of the filtration material on organic matter. In addition, humic acid is colloidal in water, and hydrogen on the surface of the active groups, such as carboxyl, hydroxyl, and carbonyl groups, can be easily dissociated, resulting in the negatively charged humic acid surface (Zhang et al. 2013). It can be seen from the zeta potential that in the micro-polluted water with neutral pH, the surface of the modified garnet media is positively charged which makes it easier to adsorb the negatively charged humic acid. At the same time, the surface of the modified garnet media is covered with Fe₂O₃, which can be

Table 3 | Adsorption capacity of different filtration media on organic matter

Raw water concentration (mg/l)	Adsorption capacity (µg/g)		
	Modified garnet media	Unmodified garnet media	Quartz sand media
4.82	2.27	0.20	0.28
10.63	5.23	0.30	0.39
20.25	11.09	0.50	0.65
29.86	17.14	0.69	0.91
39.62	22.06	1.00	1.28

Adsorption conditions: raw water volume = 100 ml, filter material volume = 50 ml, adsorption time = 3 h, speed = 100 r/min, temperature = 26 °C, pH = 7.

hydroxylated through adsorbing a layer of water molecules to form FeOOH; as a result, it can easily bind with the carboxyl, hydroxyl, and carbonyl groups on humic acid (Zhang et al. 2009). In this way, the modified garnet media has further improved the chemical adsorption effect on humic acid.

Table 3 demonstrates that the adsorption capacity of the modified media is considerably higher than that of the unmodified media. Under the same concentration of humic acid raw water, the adsorption capacity of the modified garnet media increased by 11–24 times. This result reveals that the modification with ferric chloride is an effective way to improve the adsorption properties of organic matter.

Adsorption type and adsorption isotherm

At present, Langmuir and Freundlich are the two main types of adsorption isotherms commonly used to describe adsorption in aqueous solutions. The Langmuir adsorption mode belongs to monolayer adsorption (chemical adsorption), while the Freundlich adsorption mode belongs to physical adsorption (Zhao et al. 2007a). Their corresponding linear

Table 2 | Adsorption effect of different filtration media on organic matter

Raw water concentration (mg/l)	Modified garnet media		Unmodified garnet media		Quartz sand media	
	Concentration (after adsorption) (mg/l)	Removal rate (%)	Concentration (after adsorption) (mg/l)	Removal rate (%)	Concentration (after adsorption) (mg/l)	Removal rate (%)
4.82	2.32	51.87	4.6	4.56	4.6	4.56
10.63	4.88	54.09	10.3	3.10	10.32	2.92
20.25	8.05	60.25	19.7	2.72	19.73	2.57
29.86	11.01	63.13	29.1	2.55	29.13	2.44
39.62	15.35	61.26	38.52	2.78	38.6	2.57

Adsorption conditions: raw water volume = 100 ml, filter material volume = 50 ml, adsorption time = 3 h, speed = 100 r/min, temperature = 26 °C, pH = 7.

formulae are as follows:

Langmuir adsorption linear formula: $\frac{1}{Q_e}$

$$= \frac{1}{Q_m} + \frac{1}{K_L Q_m} \cdot \frac{1}{C_e} \tag{1}$$

Freundlich adsorption linear formula: $\ln Q_e$

$$= \ln K_F + \frac{1}{n} \cdot \ln C_e \tag{2}$$

The adsorption isotherms of the three kinds of filtration media were obtained by taking the concentration of the organic matter after adsorption equilibrium as the abscissa and the adsorption capacity of the filtration media as the ordinate, as presented in Figures 7 and 8. The parameter equations of the three kinds of filtration media in the Freundlich type and Langmuir type fitting are depicted in Tables 4 and 5, respectively.

In the Freundlich fitting equation in Table 4, the K_F value is a parameter for the adsorption capacity and the intensity. The higher the K_F value, the better the adsorption performance. The K_F value of the modified garnet media is significantly higher than those of the unmodified garnet media and the quartz sand media. In the Langmuir fitting equation in Table 5, the absolute value of q_m is the maximum adsorption amount of the adsorbate on the surface of the adsorbent. The larger the absolute value, the larger the maximum adsorption amount. b is the Langmuir adsorption constant. The smaller the value, the faster the growth rate

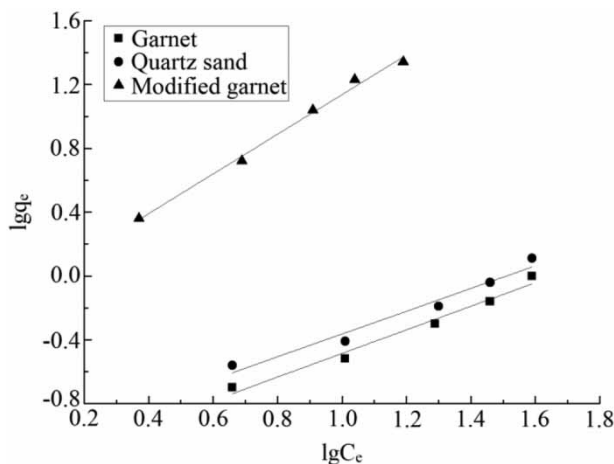


Figure 7 | Freundlich adsorption isotherm of three kinds of filtration media (Adsorption conditions: raw water volume = 100 ml, filter material volume = 50 ml, adsorption time = 3 h, speed = 100 r/min, temperature = 26 °C, pH = 7).

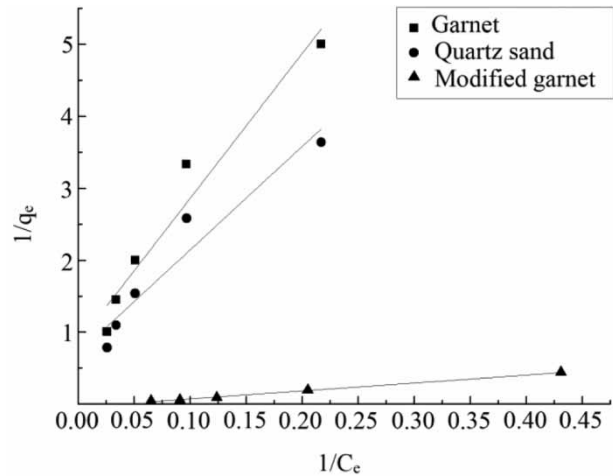


Figure 8 | Langmuir adsorption isotherm of three kinds of filtration media (Adsorption conditions: raw water volume = 100 ml, filter material volume = 50 ml, adsorption time = 3 h, speed = 100 r/min, temperature = 26 °C, pH = 7).

Table 4 | Freundlich fitting equations and correlation coefficients of three kinds of filtration media

Media	Freundlich			
	Fitting equation	K_F	$1/n$	R^2
Modified garnet	$y = 1.243x - 0.106$	0.899	1.243	0.990
Unmodified garnet	$y = 0.741x - 1.227$	0.293	0.741	0.972
Quartz sand	$y = 0.714x - 1.078$	0.340	0.714	0.957

Table 5 | Langmuir fitting equations and correlation coefficients of three kinds of filtration media

Media	Langmuir			
	Fitting equation	$ q_m $ ($\mu\text{g/g}$)	b (L/g)	R^2
Modified garnet	$y = 1.106x - 0.038$	26.316	0.034	0.997
Unmodified garnet	$y = 20.124x + 0.845$	1.183	0.042	0.938
Quartz sand media	$y = 14.371x + 0.705$	1.418	0.049	0.909

of adsorption capacity. The absolute value of q_m in the Langmuir fitting equation of the modified garnet media is much higher than those of the unmodified garnet media and quartz sand media. The value of b is also lower than those of the unmodified garnet media and quartz sand media. These values reveal that the adsorption performance of the modified garnet media is significantly improved.

A review of the presented charts reveals that the unmodified garnet media and quartz sand media have high degrees of agreement with the Freundlich equation, and the values of their correlation coefficient R^2 are 0.972 and 0.957, respectively. Meanwhile, in the Langmuir equation, the values of correlation coefficient R^2 of the two kinds of filtration media are 0.938 and 0.909, respectively. However, the modified garnet media have higher degrees of agreement with both the Langmuir equation and the Freundlich equation, with the correlation coefficients R^2 of 0.997 and 0.990, respectively. Such finding indicates that the adsorption type of the modified garnet media on the organic matter may be chemical adsorption or physical adsorption. Yet, more experiments and more advanced instruments may be needed to further investigate the adsorption type of the modified garnet media.

Dynamic filtration experiment of filter material

Removal of turbidity

The changes in turbidity of the filtered water in the modified garnet, unmodified garnet, and quartz sand filter column at a filtration rate of 8 m/h are depicted in Figure 9. A comparison of the turbidity removal by the three kinds of filter columns show the following order: the modified garnet filter column > unmodified garnet filter column > quartz sand filter column. During the filtration cycle, the average turbidity of filtered water in the modified garnet filter column was 0.40 NTU, which was 0.15 and 0.40 NTU

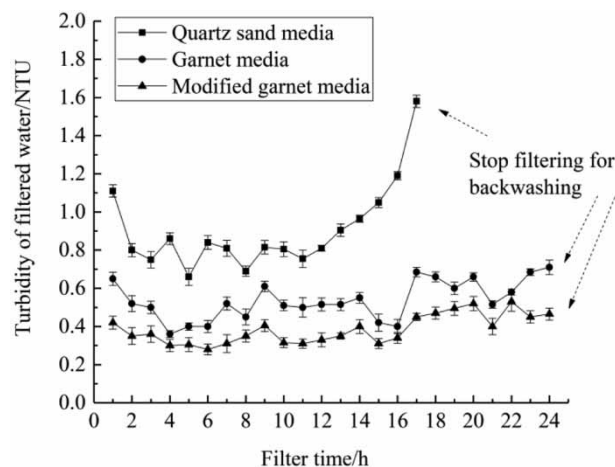


Figure 9 | Curve of turbidity of filtered water in each filter column with time.

lower than those of the unmodified garnet and quartz sand filter columns, respectively. As revealed in Figure 9, the filtration cycle of the quartz sand filter column was only 16 h at a filtration rate of 8 m/h. Moreover, the turbidity of the effluent increased significantly, and the water quality of the effluent deteriorated gradually after 11 h of filtration. However, the turbidity of the filtered water in the modified garnet filter column and unmodified garnet filter column increased only slightly, which was still much lower than 1 NTU (turbidity penetration value) after two filter columns reached the longest filtration period (24 h).

Usually, the turbidity of natural micro-polluted water includes some inorganic particles, organic particles, algae, and so on. Most of these suspended particles are negatively charged. They reach the surface of the filtration material through the migration process and deposit in the filtration material by interception and adhesion (Dentel 1988; Li et al. 2006). A small amount of PAC was added as a flocculant in the process of filtration, which destabilized some small suspended impurities and formed small flocs after a short flocculation process, which was more conducive to the interception of suspended substances by the filtration material. Typically, the unmodified garnet and quartz sand media are negatively charged, so the negatively charged suspended particles can hardly adhere onto their surface (Zhao et al. 2007b; Liu et al. 2014). The unmodified filtration materials only rely on their specific surface area and pores to physically intercept the suspended particles, which will result in the limited turbidity removal ability of the unmodified garnet or quartz sand media. The surface roughness and specific surface area of the modified garnet media are increased, which can enhance the interception of suspended particles. At the same time, in the micro-polluted water with neutral pH, the surface of the modified garnet media is positively charged, which can attract the negatively charged suspended particles in the water. In addition, the impurities deposited on the surface of the modified filtration material cannot easily fall off due to the electrostatic force, thereby further improving the turbidity removal effect.

The change in average turbidity of the filtered water with backwash times is presented in Figure 10. After six cycles of backwash, the efficiency of turbidity removal in the different filtration columns during the filtration cycle was relatively

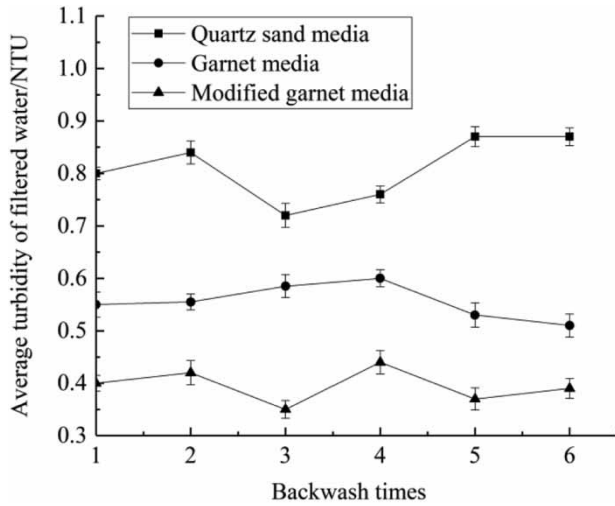


Figure 10 | Relationship between turbidity of filtered water and backwash time in each filter column.

stable, which indicated that the surface of the modified garnet filter column was bound closely with metal oxides and had good physical stability.

Removal of COD_{Mn} and UV_{254}

The changes in COD_{Mn} and UV_{254} of the filtered water in the modified garnet, unmodified garnet, and quartz sand filter column at a filtration rate of 8 m/h are presented in Figures 11 and 12, respectively. Figures 11 and 12 reveal that the COD_{Mn} and UV_{254} of the filtered water in the modified garnet, unmodified garnet, and quartz sand filter

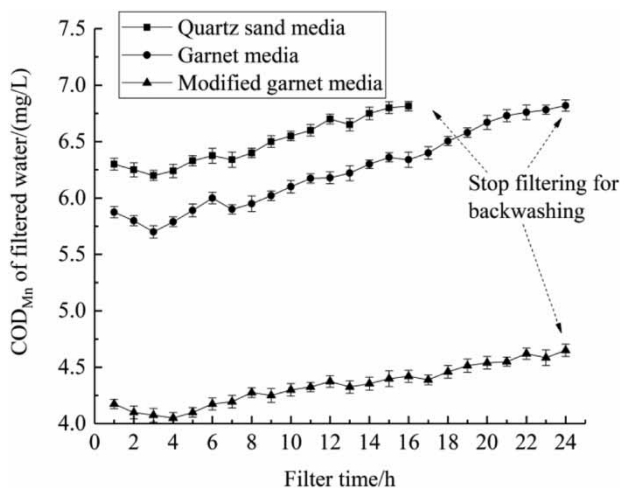


Figure 11 | Curve of removal effect of COD_{Mn} in each filter column with time.

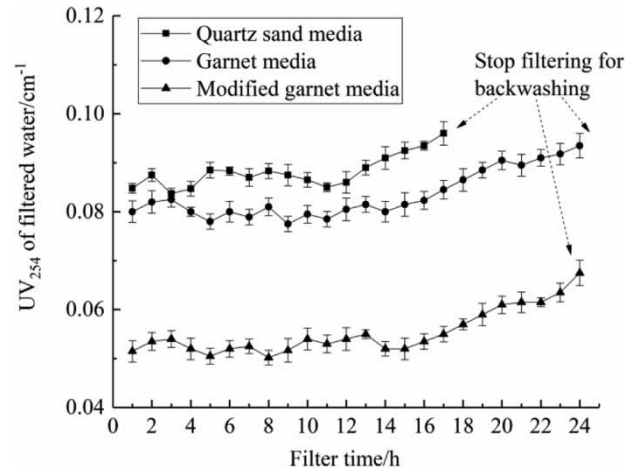


Figure 12 | Curve of removal effect of UV_{254} in each filter column with time.

columns increase slowly with the increase in filtration time. However, the removal rate of organic matter by modified garnet media is significantly higher than those of unmodified garnet and quartz sand media. During the filtration cycle, the average removal rate of COD_{Mn} by the modified garnet media was 47.7%, which was 22.9% and 25.9% higher than those of unmodified garnet and quartz sand media, respectively. The average removal rate of UV_{254} by the modified garnet media was 51.4%, which was 28% and 23.6% higher than those of unmodified garnet and quartz sand media, respectively.

A small portion of the organic matter can be wrapped outside the suspended particles and removed along with the turbidity. The functional groups of most organic substances in natural micro-polluted water are carboxyl groups, alcoholic hydroxyl groups, phenolic hydroxyl groups, and so on (Zhang et al. 2016). These functional groups tend to take off protons and are negatively charged in general. It usually needs to be removed by the adsorption of filtration material (Ma & Sheng 2002). The loading of iron oxide on the surface of garnet not only retains the filtration interception function of the garnet itself but also adds active adsorption sites on the surface of garnet, which can absorb organic matter in water while filtering. In the micro-polluted water with neutral pH, the surface of the modified garnet is positively charged which can attract the negatively charged suspended particulate matter in the water. The surface of the modified garnet media coated with positively charged iron oxide is hydroxylated by adsorbing a layer of water molecules. The surface

can exchange ions with an anionic functional group of organic substances in water. Thus, a triple removal effect of organic matter by chemical adsorption, electrostatic adsorption, and physical interception can be realized.

The changes in average COD_{Mn} and UV_{254} of filtered water with backwash times are depicted in Figures 13 and 14, respectively. In the backwashing, NaOH was added to assist the cleaning, so as to restore the organic matter removal performance of the modified garnet filter column. After six cycles of backwash, the removal of organic matter by the different filtration columns during the filtration cycle was

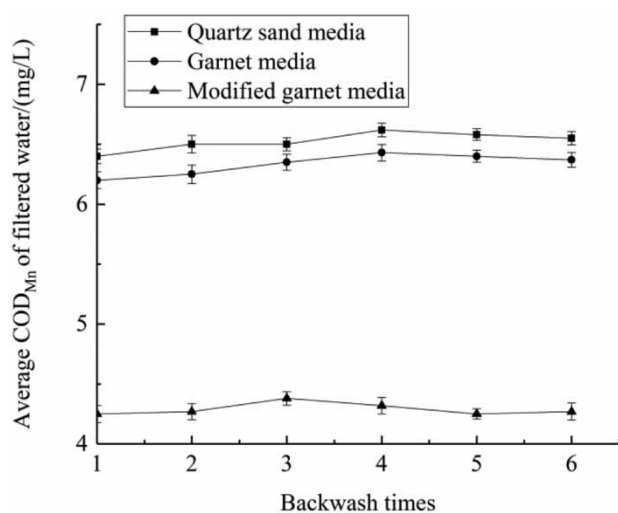


Figure 13 | Relationship between COD_{Mn} in filtered water and backwash times in each filter column.

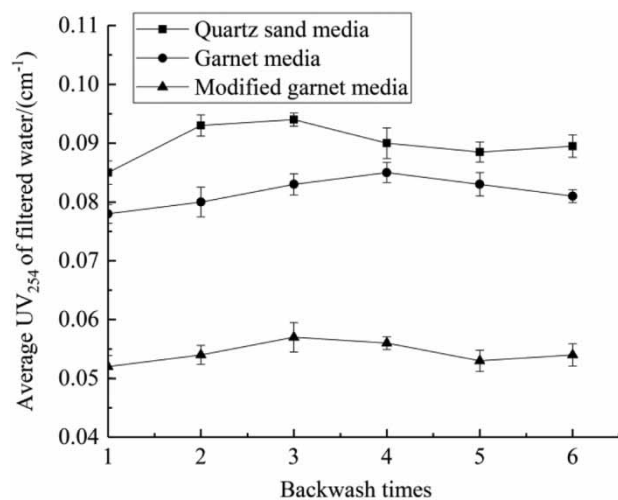


Figure 14 | Relationship between UV_{254} in filtered water and backwash times in each filter column.

relatively stable, which also indicated that the metal oxide on the surface of the modified garnet filter column was less detached under high flushing strength conditions and the physical stability of the modified garnet media was good.

CONCLUSION

In this study, the surface of garnet media was modified with ferric chloride. Characterization analysis and static adsorption experiment results revealed that compared with the smooth surface of unmodified garnet media, the surface of modified garnet media was covered with Fe_2O_3 which showed a rough concave–convex structure that has a specific area 2.44 times that of unmodified garnet media. The removal efficiency of organic matter after modification increased from 2.5–4.5% to 51.7–63.1%, and the adsorption capacity increased 11–24 times. By fitting the Freundlich isotherm equation and the Langmuir isotherm adsorption equation, the study found that the adsorption type of unmodified quartz sand and garnet media belongs to the Freundlich type, while the modified garnet media have higher degrees of agreement with both the Langmuir equation and the Freundlich equation. More experiments and more advanced instruments may be needed to further investigate the adsorption type of the modified garnet media. Results of the dynamic filtration and static adsorption experiments were consistent. In the treatment of micro-polluted water, the effect of modified garnet media on turbidity, COD_{Mn} , and UV_{254} removal was better than those of unmodified garnet media and traditional quartz sand media. After repeated backwashes, the removal performance of the modified garnet media on turbidity and organic matter remained stable.

ACKNOWLEDGEMENT

This work was supported by the Primary Research and Development Plan of Jiangsu Province (No. BE2016703), the Natural Science Youth Fund of Jiangsu Province (No. BK20171017), the National Natural Science Youth Fund of China (No. 51707093), and the Science and Technology Program of the Ministry of Housing and Urban-Rural Development of China (2014-K7-010).

REFERENCES

- Boujelben, N., Bouzid, J. & Elouear, Z. 2009 Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: study in single and binary systems. *Journal of Hazardous Materials* **163** (1), 376–382.
- Dentel, S. K. 1988 Application of the precipitation-charge neutralization model of coagulation. *Environmental Science & Technology* **22** (7), 825–832.
- Ding, C. L., Yang, X., Liu, W., Chang, Y. J. & Shang, C. 2010 Removal of natural organic matter using surfactant-modified iron oxide-coated sand. *Journal of Hazardous Materials* **174** (1), 567–572.
- Dong, F. Z. & Xu, L. 2017 Separation process of a eclogite for comprehensive utilization. *Journal of Shandong University of Technology (Natural Science Edition)* **31** (5), 70–72.
- Eisazadeh, A., Eisazadeh, H. & Kassim, K. A. 2013 Removal of Pb(II) using polyaniline composites and iron oxide coated natural sand and clay from aqueous solution. *Synthetic Metals* **171**, 56–61.
- Elbana, M., Ramírez de Cartagena, F. & Puig-Bargués, J. 2012 Effectiveness of sand media filters for removing turbidity and recovering dissolved oxygen from a reclaimed effluent used for micro-irrigation. *Agricultural Water Management* **111**, 27–33.
- GB5749-2006 2007 *Standards for Drinking Water Quality*. Standards Press of China, Beijing.
- Huang, H., Li, D. M., Lai, H. L., He, Z. Y. & Zhao, L. J. 2012 Experimental study on filtration of filter material for swimming pool sand tank by iron oxide coated sand. *Water & Wastewater Engineering* **38** (6), 92–96.
- Imai, D., Dabwan, A. H. A., Kaneco, S., Katsumata, H., Suzuki, T., Kato, T. & Ohta, K. 2009 Degradation of marine humic acids by ozone-initiated radical reactions. *Chemical Engineering Journal* **148** (2–3), 336–341.
- Li, H. Y. 2014 The harm and prevention measures of water pollution. *Applied Chemical Industry* **43** (4), 729–731 + 742.
- Li, G. H., Li, X. H. & Wang, J. B. 2006 Primary study on filtration theory of grainy filtering media. *Journal of Environmental Management College of China* **16** (1), 54–56.
- Li, D. M., He, N., Huang, H., Jiang, S. X., Liu, B. & Pang, Z. X. 2012 The study on filtration properties and backwashing efficiencies of iron oxide coated sand. *Technology Water Treatment* **38** (3), 103–106.
- Li, W., Shen, S. & Li, H. 2016 Study and optimization of the filtration performance of multi-fiber filter. *Advanced Powder Technology* **27** (2), 638–645.
- Licskó, I., Lois, L. & Szebényi, G. 1999 Tailings as a source of environmental pollution. *Water Science and Technology* **39** (10–11), 333–336.
- Liu, B., Li, D. M., Ye, T. J., Li, K. & Wang, W. H. 2014 Treatment of micro-polluted raw water by iron oxide coated sand biofilter. *China Water & Wastewater* **30** (9), 37–40.
- Liu, J., Zhang, T. & Chen, M. M. 2017 Research progress of mechanism and kinetics for removal of humic acid in micro polluted water resource. *Applied Chemical Industry* **46** (4), 744–748.
- Ma, J. & Sheng, L. 2002 Study on the effect of using iron oxide coated sand for direct filtration and its regeneration method. *China Water & Wastewater* **18** (4), 1–4.
- Matschullat, J., Borba, R. P., Deschamps, E., Figueiredo, B. R., Gabrio, T. & Schwenk, M. 2000 Human and environmental contamination in the iron quadrangle, Brazil. *Applied Geochemistry* **15** (2), 181–190.
- Verma, S., Davey, A. & Sharma, A. 2017 Slow sand filtration for water and wastewater treatment – a review. *Environmental Technology Reviews* **6** (1), 47–58.
- Wang, C. W., Deng, J. & Sun, S. Q. 2010 Study on enhanced filtration for micro-polluted surface water with PAC coated solid filter. *Journal of Hunan City University (Natural Science)* **19** (1), 23–25.
- Wang, Z. Y., Wu, H. F., He, J., Chen, R. Y., Li, X., Xue, X. R. & Wang, J. Z. 2018 Filtration and backwashing of garnet media. *Research of Environmental Sciences* **31** (9), 1620–1627.
- Yadav, S., Srivastava, V., Banerjee, S., Weng, C. H. & Sharma, Y. C. 2013 Adsorption characteristics of modified sand for the removal of hexavalent chromium ions from aqueous solutions: kinetic, thermodynamic and equilibrium studies. *Catena* **100**, 120–127.
- Zarchi, I., Friedler, E. & Rebhun, M. 2013 Polyaluminium chloride as an alternative to alum for the direct filtration of drinking water. *Environmental Technology* **34** (9), 1199–1209.
- Zhang, J. F., Zhang, H. Q. & Zhang, W. R. 2009 Surface characteristics of quartz sand coated with iron oxides. *Acta Petrologica et Mineralogica* **28** (4), 395–399.
- Zhang, Z., Shen, Z. M., Fan, T. E. & Xu, X. H. 2013 The inhibitory role of humic acid on the reduction of Cr(VI) by Fe⁰ nanoparticles and the elimination of its inhibitory role. *China Environmental Science* **33** (1), 63–68.
- Zhang, B., Zhang, K. F. & Wang, X. 2016 Filtration parameter optimization and performance research on three kinds of anthracite-sand filters. *Water & Wastewater Engineering* **42** (5), 46–51.
- Zhao, Y. H., Jia, Y. & Zhang, X. 2007a Experimental study on static adsorption of organic matter removal by modified filter media. *Journal of Shenyang Jianzhu University (Natural Science)* **23** (5), 814–817.
- Zhao, Y. H., Jia, Y. & Zhang, X. 2007b Comparison of removal efficiency of organic matter by different modified quartz sands. *China Water & Wastewater* **23** (19), 15–18.

First received 9 December 2019; accepted in revised form 7 February 2020. Available online 14 May 2020