

Research Paper

Optimization of multiple fillers used for removal of water pollutants of large well near the river in northern China

Yanjiao Gao and Shujie Li

ABSTRACT

In this paper, chromium (Cr(VI)), chemical oxygen demand (COD), and ammonia nitrogen in synthetically polluted well water were treated in three columns packed with different fillers to compare treatment effects. The concentrations of Cr(VI), COD, and ammonia nitrogen were used to investigate processing efficiency and find the most efficient column and fillers. Several effective fillers were scanned by a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) to discover the removing mechanism. Results showed No.1 column with iron powder, activated carbon, and artificial zeolite in series exerted the best ability to remove pollutants. Total removal rate of No.1 column for Cr(VI), COD, and ammonia nitrogen was 91.7%, 47.1%, and 81.6%, respectively. Iron powder removed 86.6% of Cr(VI), activated carbon removed 30.1% of COD, and artificial zeolite removed 66.9% of ammonia nitrogen. The ability of iron powder to remove Cr(VI) is attributed to the redox reaction between iron powder and Cr(VI). Removal of COD by activated carbon is based on the adsorption of activated carbon. Artificial zeolite contains a variety of cationic components and is capable of removing ammonia nitrogen from the water by ion exchange. The No.1 column process has higher reference values for the pretreatment of polluted well water in the towns of underdeveloped countries.

Key words | ammonia nitrogen, chemical oxygen demand, hexavalent chromium, large well water, multiple fillers

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INTRODUCTION

With about 20% of the world's population China only has 5–7% of global freshwater resources (Qiu 2010). Especially in the north of China, water supply relies heavily on groundwater due to the lack of surface water resources. According to the Groundwater Pollution and Control Plan of China (2011–2020), 65% of domestic water, 50% of industrial water, and 33% of agricultural water in the north of China come from groundwater resources. The proportion of groundwater used for drinking in the Liao River Basin of the northeast of China is higher than that of other areas.

Usually, drinking water is extracted from groundwater by means of setting up large open wells near the river. The

advantage of this is that a certain amount of river water can penetrate into large wells to replenish groundwater, so many villages and towns use large open wells near the river to provide water. However, with the rapid development of China's economy, the degree of water pollution has also increased, and the water quality of large open wells near the river in some areas has been seriously affected. Agricultural sources and rivers that accept the disorderly discharge of domestic sewage and industrial waste water are responsible for the water pollutants in large wells. The main pollutants in groundwater include organic matter (Kong *et al.* 2016), heavy metals (Li *et al.* 2015;

doi: 10.2166/washdev.2019.014

Kennedy *et al.* 2018; Vatandoost *et al.* 2018), and nitrogen (Højberg *et al.* 2017). In northern China, the concentrations of heavy metals, nitrogen, and organic matter in contaminated groundwater have ranged from tens of micrograms to tens of milligrams according to the literature (Gu *et al.* 2013; Huang *et al.* 2015; Liu *et al.* 2015). In the past, groundwater quality was good and it was only necessary to disinfect groundwater for drinking. But now simple disinfection cannot control the problem of well water pollution, and people are trying to find efficient ways to dispose of polluted water from rural wells.

A common method for the treatment of groundwater for drinking is membrane filtration, such as microfiltration (MF) or ultrafiltration (UF) (Metsämuuronen *et al.* 2014; Kasim *et al.* 2016). As a type of drinking water treatment method, low-pressure MF and UF can effectively remove turbidity, organic matter, pathogens, and disinfection by-products (DBPs). MF and UF have the advantage of low energy consumption, no pollution to the environment, and are easy to automate (Knappett *et al.* 2011; Palit 2015). However, the water quality of the large open wells near the river is seriously affected by polluted rivers, and thus cannot be directly applied to the MF or UF membrane, otherwise the membrane will be contaminated and deteriorate. Therefore, it is necessary to reduce the concentration of pollutants in the wells before using membrane treatment method.

Membrane pretreatment technologies mainly include coagulation (Jung *et al.* 2015), precipitation and flotation (Xu & Narbaitz 2016), granular activated carbon adsorption (Gur-Reznik *et al.* 2008), and pre-oxidation (Wang *et al.* 2013). Coagulation as a pretreatment process of the membrane method can facilitate the collision and aggregation of colloidal particles in water, improve the sedimentation efficiency, and has a low cost and relatively simple operation. It is a common method for removing pollutants from drinking water (Xiangli *et al.* 2008; Huang *et al.* 2009). Precipitation and flotation can be used to remove natural organic matters (NOM) from water before using hollow fiber UF membrane to treat water (Xu & Narbaitz 2016). Adsorption of granular or powdered activated carbon is also a pretreatment technology before the membrane (Huang *et al.* 2009). Activated carbon has a relatively large specific surface area to adsorb soluble non-polar organics in water (Stoquart *et al.* 2012). Although the

adsorption capacity of activated carbon is low and the adsorption kinetics are slow, it is capable of adsorbing hydrophobic organic compounds at lower concentrations (Matsushita *et al.* 2013). Pre-oxidation is also used for water pretreatment and the oxidants are ozone, permanganate, and chlorine.

However, the choice of pretreatment technology should be based on water quality conditions and local economic levels. The water quality parameters are more complicated in the large open wells of rural northeast China, and the main pollutants include heavy metals, organic matter, and ammonia nitrogen. In addition, it is necessary to consider the poor economic conditions in China's villages and towns, and adopting a pre-processing method with less investment and easy operation and management is a benefit for local people. This study considered the use of multiple fillers to remove common heavy metal Cr(VI), chemical oxygen demand (COD), and ammonia nitrogen. Some fillers were selected for the continuous running experiment of the columns, and the best filler combination was selected to study the treatment effects on the three pollutants; the removal mechanism was also analyzed. This study has certain reference values for the pretreatment of small drinking water wells in rural areas of some developing countries.

MATERIALS AND METHODS

Fillers

The fillers used in the experiment were iron powder, activated carbon, artificial zeolite, iron-carbon, and quartz sand. The specific physical properties of these fillers are shown in Table 1.

Chemicals

The analytically pure chemical reagents used in the experiment included potassium dichromate ($K_2Cr_2O_7$), ammonium chloride (NH_4Cl), glucose ($C_6H_{12}O_6$), manganese dioxide (MnO_2), sodium potassium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$), Nessler's reagent, and hexavalent chromium detecting reagent.

Table 1 | Physical properties of fillers

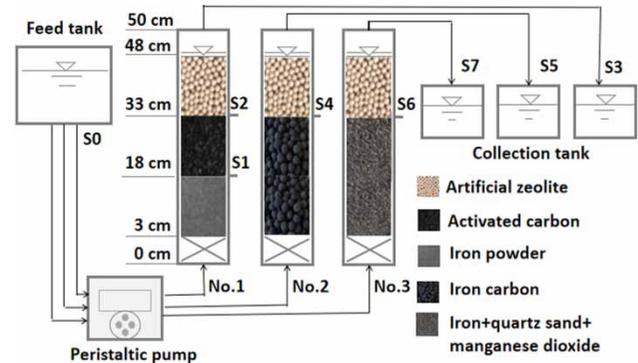
Filler name	Particle size (mm)	Other properties
Iron powder	0.4–0.5	Si ≤ 0.79%, C ≤ 8.62%
Activated carbon	3–5	Specific surface area 1,000–1,600 m ² /g, iodine adsorption value 1,230 mg/g
Artificial zeolite	4–5	Calcium ion exchange capacity ≥20 mg/g
Iron-carbon	7–8	Specific surface area 1.2 m ² /g, specific weight 1.0 g/cm ³ , Fe = 75–85%, C = 10–20%
Quartz sand	1–2	Specific weight 2.65 g/cm ³

Water samples

The water samples in the laboratory were prepared by adding chemical pollutants into underground clean well water (did not contain Cr(VI), ammonia nitrogen, and COD), and the clean water quality met the requirement of the national sanitary standards for drinking water. Potassium dichromate, ammonium chloride, and glucose were used as sources of pollution to be added to clean well water to simulate Cr(VI), ammonia nitrogen, and organic pollution. The pH of raw water was from 6.4 to 7.0, and water temperature was 20–25 °C. The initial concentrations of Cr(VI), ammonia nitrogen, and COD were 10 mg/L, 20 mg/L, and 100 mg/L, respectively.

Experimental setup and operating method

Figure 1 shows the experimental setup. Three identical plexi-glass columns (internal diameter = 5 cm, height = 50 cm, volume = 981 cm³) with different combinations of fillers were used to dispose of polluted water. No.1 column was loaded with three kinds of fillers, iron powder (740 g), activated carbon (145 g), and artificial zeolite (210 g) from bottom to top. No.2 column was filled with two kinds of fillers, iron-carbon (993 g) below and artificial zeolite (210 g) on the top. A mixture of iron powder (1,530 g), quartz sand (286 g), and manganese dioxide (400 g) was used to fill the bottom of No.3 column and artificial zeolite (210 g) was on the top. There were four sampling ports in different parts of the columns, and also an inlet sampling point and

**Figure 1** | Schematic diagram of the water treatment system.

three outlet sampling points. The system was equipped with a feed tank (volume = 100 L) and three collection tanks (each volume = 50 L). A five-channel peristaltic pump (BT200M, MC4X-5 pump head, 0.1–200 rpm, flow rate 0.0249–49.8 mL/min) was used to supply waste water for the columns; the inlet flow of columns could be controlled by adjusting the speed of the pump. The three columns were supplied with the same polluted water from the feed tank at a flow rate of 10 L/min. The concentrations of Cr(VI), COD, and ammonia nitrogen in the water samples from seven sampling points, S1 to S7, were measured every other day. The surface properties of the original fillers were scanned using SEM with energy dispersive spectrometer (EDS), and after the reaction the fillers were also determined for comparison.

Testing instruments and analytical methods

Table 2 depicts the test instruments and analytical methods used in the experiment to detect Cr(VI), ammonia nitrogen, COD, pH, and surface morphology and element types.

RESULTS AND DISCUSSION

Removal effects of fillers on pollutants in No.1 column

To investigate the effects of iron powder, activated carbon, and artificial zeolite in No.1 column on the Cr(VI), COD, and ammonia nitrogen removal performance, the concentrations of Cr(VI), COD, and ammonia nitrogen of water

Table 2 | Water quality parameter test methods and instruments used

Water quality parameters	Test instruments	Analytical methods
Cr(VI)	Microcomputer hexavalent chromium analyzer (HI96723)	Diphenylcarbazide spectrophotometry
Ammonia nitrogen	Visible spectrophotometer (722N)	Nessler reagent spectrophotometry
COD	COD analyzer (ET1151M) and multi-function digestion device (ET3150B)	Digestion spectrophotometry
pH	pH meter (pHS – 25)	Electrode method
Surface morphology and element types	SEM with EDS (Hitachi company)	Energy dispersive spectrometer

samples from three different sampling ports S1, S2, and S3 were determined and results are plotted in Figures 2–4.

Figure 2 shows results of the effluent Cr(VI) concentrations of S1, S2, and S3 in No.1 column with time interval from 1 d to 30 d. Results showed that the concentrations of Cr(VI) at S1 changed from 1.22 mg/L to 1.40 mg/L, and the average Cr(VI) concentration was 1.34 mg/L. From the curve of S1, the effluent concentration of Cr(VI) did not increase significantly with increasing time, and the average removal rate of Cr(VI) was stable at 86.6% due to the chemical reduction of iron powder on Cr(VI). The concentration results of S2 indicated that Cr(VI) concentrations varied between 0.87 and 1.19 mg/L with increasing time, and an average concentration of 1.02 mg/L was obtained. The activated carbon removed only 3.2% of Cr(VI) on average, and this could be related to the competitive adsorption and selective adsorption of different types of activated carbon. From the curve of S3, the removal ability of artificial zeolite to Cr(VI) was also very weak; only Cr(VI) average removal rate of 1.9% was

achieved, which was due to the poor selectivity of zeolite for the exchange and adsorption capacity of Cr(VI). After passing through three kinds of filter materials, the average Cr(VI) concentration was reduced to 0.83 mg/L, and the corresponding average removal rate of No.1 column was 91.7%. The removal capacity of Cr(VI) by three kinds of fillers in No.1 column was arranged in descending order as iron, activated carbon, artificial zeolite.

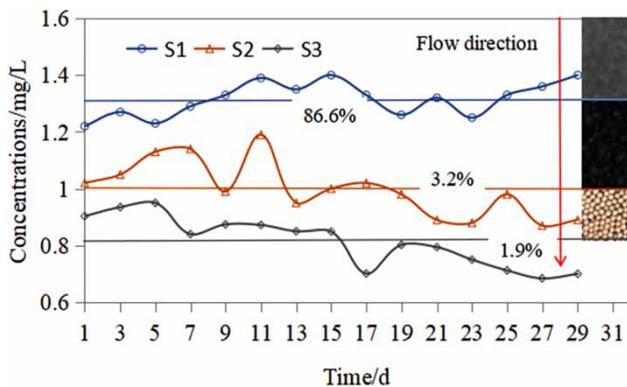


Figure 2 | Cr(VI) concentrations of S1–S3 changing with increasing time in No.1 column.

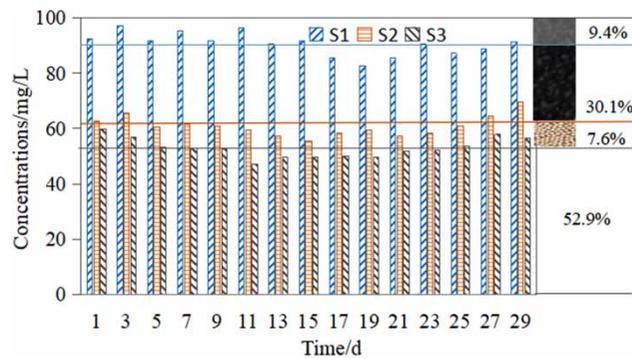


Figure 3 | COD concentration of S1–S3 changing with increasing time in No.1 column.

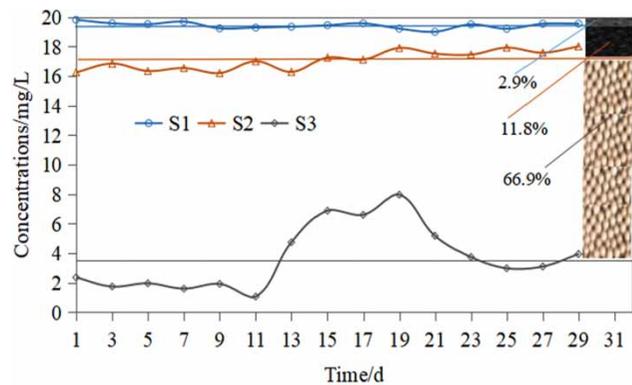


Figure 4 | Ammonia nitrogen COD concentration of S1–S3 changing with increasing time in No.1 column.

Xu *et al.* (2014) synthesized nanoscale zero-valent iron supported on activated carbon (NZVI/AC) to remove Cr(VI) with an initial concentration of 10 mg/L (the same as this experiment), under pH = 5, t = 60 min, T = 25 °C, and NZVI loading = 25%. A removal rate of 94% Cr(VI) was obtained and it was higher than the removal rate of 86.6% (t = 7 d, in Figure 2) in No.1 column of this experiment. It can be seen that carbon-supported nano-iron could improve the treatment effect of Cr(VI). However, the iron/activated carbon/zeolite process in this paper does not need to adjust the original pH before the reaction, and it can be economically applied to underdeveloped rural areas.

The COD concentrations changing with time at the S1–S3 points are presented in Figure 3. Figure 3 reveals that the average removal rate of COD by the combined fillers of No.2 column was 41.7% and it was not very high. The activated carbon was responsible for removing 30.1% of the COD, and the removal rates of COD by iron powder and zeolite were 9.4% and 7.6%, respectively. The ranges of COD concentrations and average values of COD at S1, S2, and S3 were 82.61–97.35 mg/L, 55.65–69.61 mg/L, 47.32–57.94 mg/L and 90.64 mg/L, 60.53 mg/L, 52.92 mg/L, respectively. No.1 column combining iron powder, activated carbon, and artificial zeolite removed a total of 47.1% of COD. Compared with the three fillers, activated carbon had the strongest ability to remove COD, iron powder was second, and artificial zeolite last. In the research of Kaleta *et al.* (2017), powdery activated carbon was adopted to determine the effectiveness of the removal of humic substances (total organic carbon, TOC = 14–20 mg/L) from underground water. The rate of TOC decreased by 29–40%, which was close to the COD removal rate of 30.1% by activated carbon in No.1 column of this experiment. The removal of organic matter by activated carbon is solely due to adsorption, and there is a problem of adsorption capacity. Therefore, the removal rate of organic matter (COD) is not particularly high, and it is necessary to cooperate with other processes, such as ultrafiltration technology, to further purify organic pollutants.

In Figure 4, the concentrations and average values of effluent ammonia nitrogen in S1, S2, and S3 were 19.05–19.81 mg/L, 16.27–18.05 mg/L, 1.10–7.93 mg/L and 19.42 mg/L, 17.06 mg/L, 3.68 mg/L, respectively. The removal capacity of iron powder, activated carbon, and

artificial zeolite on ammonia nitrogen was 2.9%, 11.8%, and 66.9%, respectively. No.1 column with all the fillers removed a total of 81.6% of ammonia nitrogen. During the 30-day operation of No.1 column, the removal of ammonia nitrogen by zeolite was at first stable, then decreased, and then increased due to the replacement of the zeolite as the removal rate decreased. From curve S3 we can see the efficiency of zeolite removal of ammonia nitrogen was stable within 11 days, but from the 12th to the 19th day, the effluent concentration of ammonia nitrogen began to rise, and the efficiency of zeolite removal of ammonia nitrogen decreased, which was due to the adsorption exchange capacity of zeolite tending to be saturated. After the replacement of the zeolite filler, the effluent concentrations of ammonia nitrogen began to decrease, and the removal rate rose again. In short, the removal of ammonia nitrogen by artificial zeolite was best, the activated carbon was poor, and the iron powder had almost no removal ability. Zeolite acting as an *in-situ* filler has been used more for the removal of groundwater contaminants, especially for the removal of ammonia nitrogen by ion exchange effect. Li *et al.* (2014) designed a pilot-scale PRB (permeable reaction barrier) to achieve sustainable use of zeolite in removing ammonium through sequential nitrification, adsorption, and denitrification under the condition of adding an oxygen-releasing compound in the upper layers of the zeolite; during the long-term operation (328 days), more than 90% of ammonium was consistently removed. The ammonia removal mechanism is more dependent on the role of microorganisms, and is suitable for *in-situ* groundwater ammonia nitrogen pollution degradation. In the experiments in this paper, zeolite removal of ammonia nitrogen mainly relies on the ion exchange adsorption between zeolite and ammonia, which is faster and suitable for the treatment of productive water.

Removal effects of fillers on pollutants in No.2 column

In order to investigate the effects of iron-carbon and artificial zeolite in No.2 column on the Cr(VI), COD, and ammonia nitrogen removal performance, the concentrations of Cr(VI), COD, and ammonia nitrogen of water samples from S4 and S5 points were measured and the results are shown in Figures 5–7.

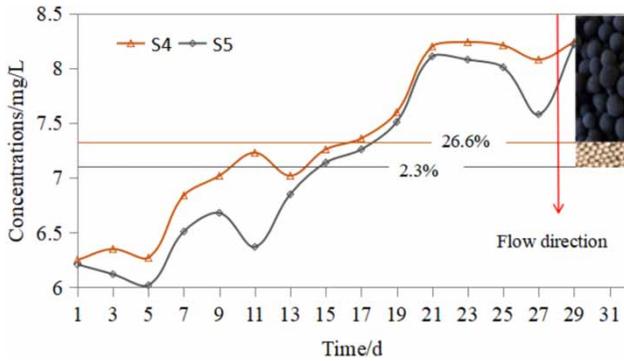


Figure 5 | Cr(VI) concentrations of S4 and S5 changing with increasing time in No.2 column.

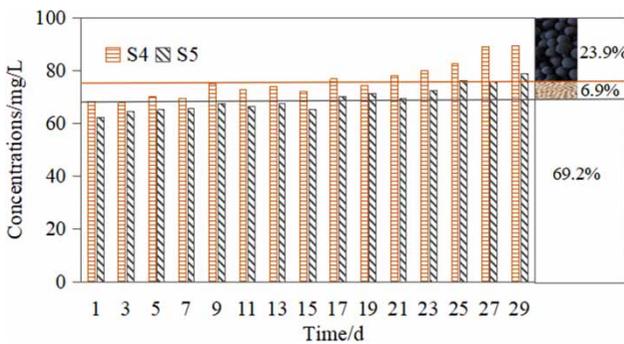


Figure 6 | COD concentration of S4 and S5 changing with increasing time in No.2 column.

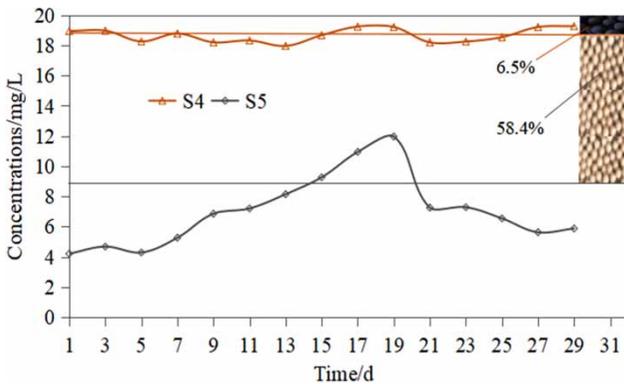


Figure 7 | Ammonia nitrogen concentration of S4 and S5 changing with increasing time in No.2 column.

The Cr(VI) concentration curves of S4 and S5 are presented in Figure 5. The concentration of Cr(VI) at point S4 varied from 6.25 to 8.24 mg/L, and the average Cr(VI) concentration was 7.34 mg/L during the water running time of No.2 column. The average removal rate of Cr(VI) by the iron-carbon segment was 26.6%; however, from

curve S4, under the removal of iron-carbon, the effluent concentration of Cr(VI) increased with time, and the removal effect was unstable. It can be stated that the effect of iron-carbon in removing Cr(VI) was worse than that of iron in removing Cr(VI), which may be related to environmental conditions, such as appropriate pH. The concentration of Cr(VI) at point S5 changed from 6.02 mg/L to 8.22 mg/L, and the average concentration of Cr(VI) was 7.11 mg/L. The average removal rate of Cr(VI) in the zeolite segment was 2.3% when the column device was operated for 30 days. The removal rate of Cr(VI) by the entire fillers of No.2 column was 28.9%. Compared with No.1 column, the removal ability of iron-carbon was significantly smaller than that of iron powder for Cr(VI).

Figure 6 shows the COD concentrations of S4–S5 versus time. The concentration of effluent COD at S4 point varied from 67.91 to 89.44 mg/L, the average concentration was 76.12 mg/L, and the average removal rate of the iron-carbon segment to COD was 23.9%. With the column device operating for 30 days the removal ability obviously declined, which indicated that iron-carbon can remove COD, but was affected by environmental conditions. It may be related to pH. The pH of the whole reaction is increasing. Moreover, the removal effect of iron-carbon on COD was less than that of activated carbon in No.1 column. The concentration of effluent COD at the S5 point varied from 62.36 to 78.90 mg/L, the average concentration was 69.25 mg/L, and the average removal rate of COD in the zeolite segment was 6.9%; with 30 day operating time the removal capacity decreased significantly. This showed that zeolite has limited ability to remove COD. The COD removal rate of the entire No.2 column was 31.8%.

The S4 curve in Figure 7 shows the concentration of ammonia nitrogen varied from 17.96 to 19.27 mg/L, and the average ammonia nitrogen concentration was 18.70 mg/L. Curve S5 showed the concentration of ammonia nitrogen varied from 4.20 to 1.96 mg/L, and the average concentration was 7.02 mg/L. The average removal rate of ammonia nitrogen by the iron-carbon segment was 6.5%, which was much lower than the average 58.4% removal rate by the zeolite segment. The removal rate of ammonia nitrogen by the entire fillers of No.2 column was 64.9%. The results of Figure 7 indicate that iron-carbon was not the

best choice for ammonia nitrogen treatment but artificial zeolite exhibited a good ability to remove ammonia nitrogen.

Compared with No.1 column, No.2 column used a special iron-carbon integrated ball filler, which can produce an iron-carbon microelectrolysis effect to remove the organic matter. However, for the removal of Cr(VI), the redox effect between iron and Cr(VI) is still exerted, while the removal effect of iron carbon on ammonia nitrogen was poor. Huang *et al.* (2017) used an activated carbon and cast iron combined system to remove Cr(VI) in groundwater, which showed that Cr(VI) can be reduced to Cr(III) coupled with the oxidation of Fe(0) to Fe(II) due to the effect of galvanic interaction and direct electron transfer from Fe(0) to Cr(VI) in this combined system. This is consistent with the mechanism of iron-carbon removal of Cr(VI) in No.2 column of this experiment.

Removal effects of fillers on pollutants in No.3 column

The filler packed in the lower part of No.3 column was a mixture of iron powder, manganese dioxide, and quartz sand, and the top was filled with zeolite. The concentration changes of Cr(VI), COD, and ammonia nitrogen in S6 and S7 sampling ports were investigated. The experimental results are shown in Figures 8–10.

The data in Figure 8 indicate the concentration of Cr(VI) at point S6 varied from 1.52 to 4.89 mg/L, and the average concentration was 3.05 mg/L. The concentration of Cr(VI)

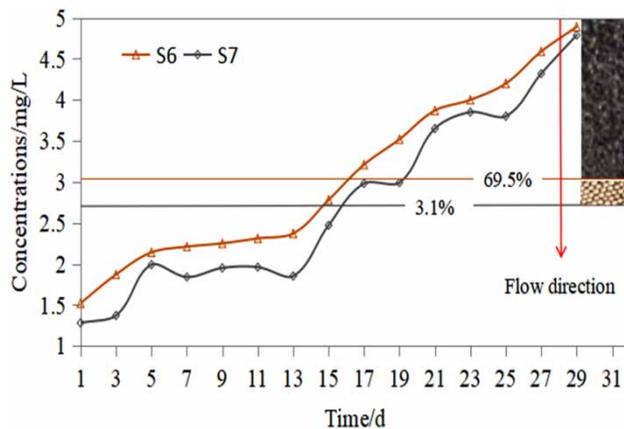


Figure 8 | Cr(VI) concentrations of S6 and S7 changing with increasing time in No.3 column.

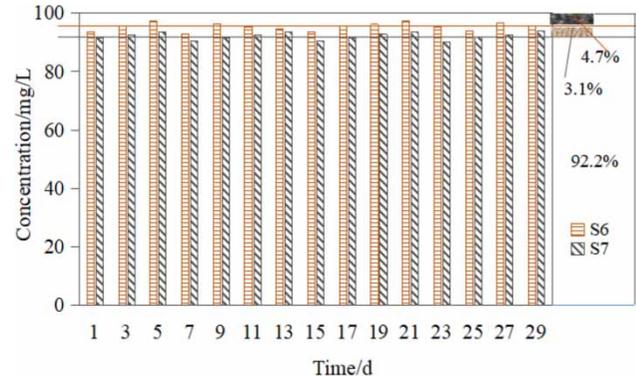


Figure 9 | COD concentration of S6 and S7 changing with increasing time in No.3 column.

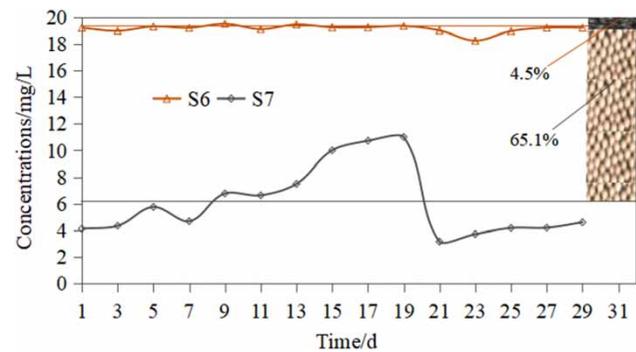


Figure 10 | Ammonia nitrogen concentration of S6 and S7 changing with time increasing in No.3 column.

at point S7 varied from 1.28 to 4.79 mg/L, and the average concentration was 2.74 mg/L. The average removal rate of the mixture of iron powder, manganese dioxide, and quartz sand on Cr(VI) was 69.5%, and it was much higher than 3.1% of the removal rate of Cr(VI) by the zeolite segment. The removal rate of the mixing segment was lower than the removal rate of the iron powder section of the No.1 column, which is due to the low iron content, but the purpose of adding manganese dioxide was to improve the catalytic effect, and the quartz sand was added to prevent iron powder blockage after long-term operation of the column. No.3 column achieved a total removal effect of 72.6% on Cr(VI) by the entire fillers.

The mixed filler of iron powder, manganese dioxide, and quartz sand and the artificial zeolite in Figure 9 were not ideal materials for COD removal. The average removal rate of the mixed fillers was 4.7%, and that of the zeolite was only 3.5%. The effluent COD concentration

of S7 in No.3 column varied from 90.27 to 93.83 mg/L, and only 7.8% of COD removal rate was obtained by the entire fillers. The results showed that the mixed fillers removal of COD relied on a small part of mechanical retention, and the zeolite selectively adsorbed ammonia nitrogen instead of COD.

It can be seen from Figure 10 that the main effect of the removal of ammonia nitrogen in No.3 column was still attributed to the artificial zeolite, which achieved a removal rate of 65.1%, and S7 average concentration of No.3 column was reduced to 6.08 mg/L. In No.3 column, the mixed fillers achieved only a removal rate of 4.5% for ammonia nitrogen, and total ammonia nitrogen removal rate reached 69.6%.

Comparison of the treatment effects of three columns on pollutants

Among the three columns, there were five kinds of fillers, iron powder (Fe), activated carbon (C), iron-carbon (Fe + C), iron powder + manganese dioxide + quartz sand (Fe + Mn + sand), and artificial zeolite. Table 3 compares the removal rates of Cr(VI), ammonia nitrogen, and COD by the five kinds of fillers in the three columns. The order of removal ability of Cr(VI) was Fe > Fe + Mn + sand > Fe + C > C > artificial zeolite. The order of removal capacity of COD was C > Fe + C > Fe > artificial zeolite > Fe + Mn + sand. The order of removal of ammonia nitrogen was artificial zeolite > C > Fe + C > Fe + Mn + sand > Fe. Therefore, the three fillers, iron powder,

activated carbon, and artificial zeolite of No.1 column were suitable for treating three pollutants, and this combination was the most reasonable for effectively removing complex pollution of Cr(VI), COD, and ammonia nitrogen from wells near the river.

Analysis of EDS elements detecting results

In order to investigate what changes have occurred in the chemical elements on the surface of fillers before and after water treatment and to infer which chemical reactions occurred, the surface of fillers in No.1 column were scanned by SEM with EDS.

Figures 11 and 12 show the EDS scanning results of the iron powder surface before and after the reaction. According to the two figures, there were the four elements of C, O, Fe, and Si on the surface of the iron powder before the reaction, but then after the reaction, K, N, and Cr occurred as well and Si had disappeared. The appearance of Cr indicated that chemical reactions take place between Fe(0) and Cr(VI) so that the element Cr was transferred to the surface of the iron powder. Fe(0) can corrode in water and consume hydrogen ions. In the presence of Cr(VI), Fe(0) can undergo redox reactions with Cr(VI), and there was a two-step reaction between them (Gheju 2011):

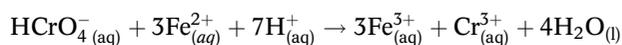
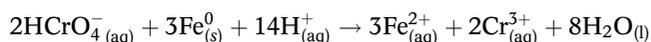


Table 3 | Comparison of removal effects of different fillers

Parameters	Column number	Removal rate of pollutants by different fillers/%					
		Fe	C	Fe + C	Fe + Mn + sand	Zeolite	
Cr(VI)/mg/L	1	86.6	3.2	–	–	1.9	Average 2.4
	2	–	–	26.6	–	2.3	
	3	–	–	–	69.5	3.1	
COD/mg/L	1	9.4	30.1	–	–	7.6	Average 5.9
	2	–	–	23.9	–	6.9	
	3	–	–	–	4.7	3.1	
Ammonia nitrogen/mg/L	1	2.9	11.8	–	–	66.9	Average 63.5
	2	–	–	6.5	–	58.4	
	3	–	–	–	4.5	65.1	

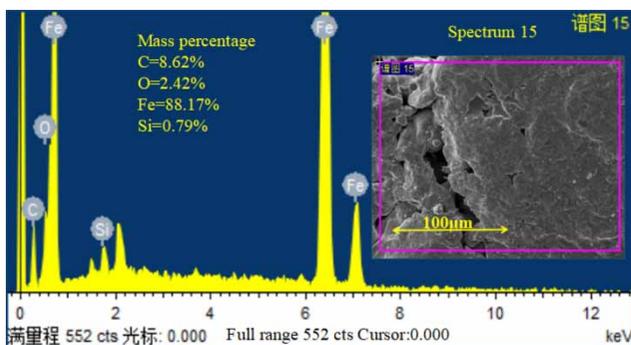


Figure 11 | EDS analysis image of iron powder before reaction.

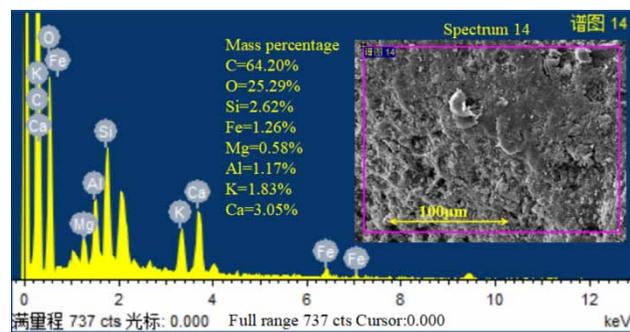


Figure 13 | EDS analysis image of activated carbon before reaction.

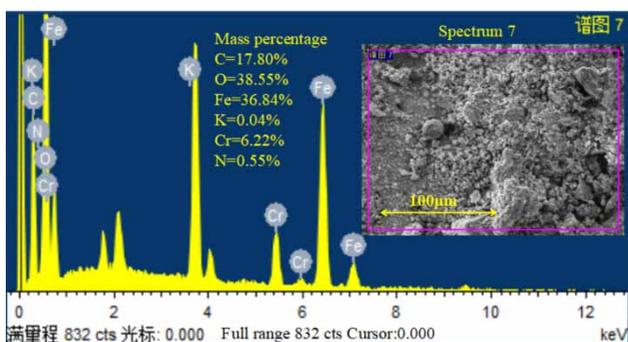


Figure 12 | EDS analysis image of iron powder after reaction.

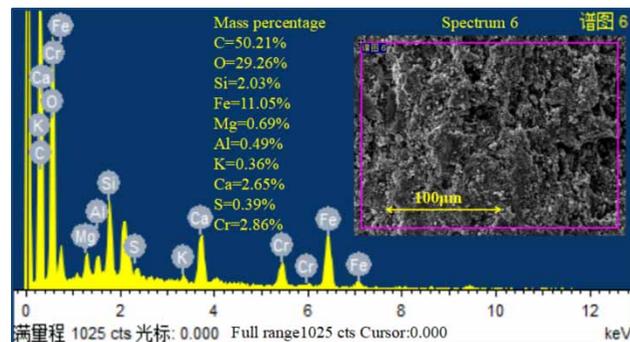
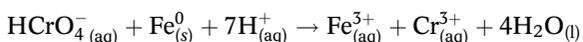


Figure 14 | EDS analysis image of activated carbon after reaction.

The overall reaction equation is as follows:



In this reaction, iron is oxidized to ferric iron as a reducing agent, and Cr(VI) is reduced as an oxidizing agent to Cr(III) which is less toxic. Studies have shown that the reaction produces co-oxides or hydroxides of Cr(III) and ferric iron (Ai *et al.* 2008; Fiuza *et al.* 2010; Gheju 2011). Blowes *et al.* (1997) indicated that the resulting Cr(III) was removed either through the formation of a solid (Fe(III)–Cr(III) (oxy) hydroxides) or by adsorption of Cr(III) onto the goethite surface. The N element was detected on the surface of the iron powder, which indicated that ammonia nitrogen was adsorbed onto the iron powder. Generally speaking, Fe(0) did not chemically react with ammonia nitrogen. The change in the state of the Si and K elements in the solution and the iron powder was due to the ion exchange of the components in the iron powder.

Figures 13 and 14 are EDS analysis diagrams of activated carbon before and after water treatment,

respectively. From Figures 13 and 14, it is known that there were eight elements before the reaction, and the S and Cr elements were obtained after the reaction. Cr was derived from the adsorption of Cr(VI) in the water sample by activated carbon and S was from the adsorption of sulfate in the water sample by activated carbon. Activated carbon has a poor adsorption capacity for Cr(VI), but good adsorption for COD, because activated carbon is a selective adsorption that is related to competitive adsorption and the type of carbon. For activated carbon with poor capacity, modification can be considered, such as acid modification. In this experiment, considering the economic and environmental aspects, there is no modification of activated carbon, which avoids secondary pollution and cost increase caused by modified materials.

As shown in Figure 15, seven kinds of elements, C, O, Fe, Si, Mg, Al, and Na were detected by EDS on the surface of the unreacted artificial zeolite. The artificial zeolite was synthesized by mainly mixing Na_2O , Al_2O_3 ,

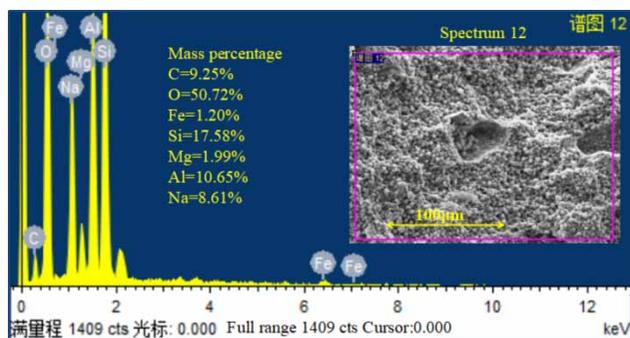


Figure 15 | EDS analysis image of artificial zeolite before reaction.

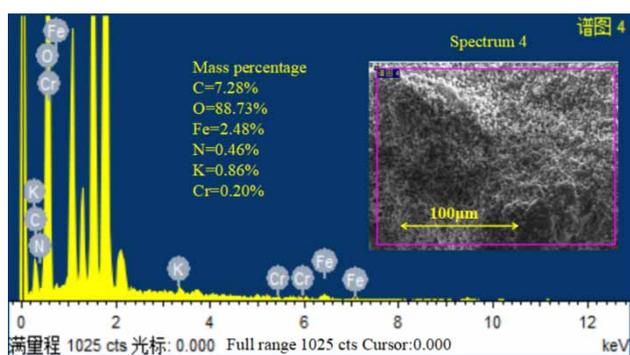


Figure 16 | EDS analysis image of artificial zeolite after reaction.

SiO_2 , and H_2O in a specific ratio to form a gelling substance, which was crystallized and heated to give a finished product. The molecular formula of the artificial zeolite was $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$. In Figure 16, after treatment with water, the elemental species on the surface of the artificial zeolite became C, O, Fe, N, K, Cr. The removal mechanism of artificial zeolite on pollutants mainly depended on adsorption and ion exchange and cations such as Si, Mg, Al, Na can be exchanged with N, K, Cr cations in water. N came from ammonia nitrogen in source water, Cr was derived from Cr(VI), and K was derived from raw water. This exchange effect proved that the artificial zeolite can be exchanged for the removal of Cr(VI) and ammonia nitrogen. The artificial zeolite had a cage structure with well-developed pores formed by bridging a silicon oxytetrahedron and an aluminum oxytetrahedron. This structure facilitated adsorption and ion exchange.

CONCLUSIONS

In this study, three columns equipped with five different fillers of iron powder, activated carbon, artificial zeolite,

iron-carbon, and quartz sand were operated at a constant hydraulic flow rate of 10 mL/min to remove the combined pollution of Cr(VI), COD, and ammonia nitrogen in large well synthetic water samples near the river. No.1 column connected the iron powder, activated carbon, and artificial zeolite in series, which resulted in the effective removal of the three pollutants with an average removal rate for Cr(VI), COD, and ammonia of 91.7%, 47.1%, and 81.6%, respectively. The removal mechanisms on pollutants by these fillers are mainly the oxidation of iron, the adsorption of activated carbon, and the ion exchange of zeolite on Cr(VI), COD, and ammonia nitrogen. SEM images and EDS analysis also explained the occurrence of these mechanisms on the surface of the fillers. For well water pretreatment, iron powder, activated carbon, and artificial zeolite series process can effectively reduce the content of Cr(VI), COD, and ammonia pollutants, and reduce the burden of membrane pollution for the subsequent ultrafiltration or microfiltration process. This process will have good application value for well water pretreatment in underdeveloped areas.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support for this work (No. 51308274) provided by Natural Science Foundation of China.

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