

# Fe and Mn removal from mining drainage using goaf filling materials obtained from coal mining process

Liping Zhang, Aolei Chen, Hongbin Qu, Shouqiang Xu, Xue Zhang and Xuwen He

## ABSTRACT

Coal gangue, sandy soil and clay (mass ratio 45:4:1) as goaf filling materials acquired from coal mining processes were applied to remove Fe and Mn effectively from mining drainage. The results of an adsorption kinetic study showed that the Fe adsorption equation was  $y = 21.454x + 8.4712$ ,  $R^2 = 0.9924$  and the Mn adsorption equation was  $y = 7.5409x + 0.905$ ,  $R^2 = 0.9957$ . Meanwhile, the goaf filling materials had low desorption capacity (Fe 6.765  $\mu\text{g/g}$ , Mn 1.52  $\mu\text{g/g}$ ) and desorption ratio (Fe 8.98%, Mn 11.04%). Experiments demonstrated that Fe and Mn from mining drainage could be removed stably at a flow rate of 1.2 L/min, Fe inlet concentration of less than 40 mg/L, Mn inlet concentration of less than 2 mg/L and neutral or alkaline conditions. During a procedure of continuous experiments, the effluent quality could meet the requirement of the 'Code for Engineering Design of Sewage Regeneration-GB503352-2002'. A real-application project using goaf filling materials to treat mining drainage in Shendong coal mine showed that the average cost per ton of mining drainage was about 0.55 RMB, which could bring about considerable economic benefit for coal mining enterprises.

**Key words** | adsorption and desorption, goaf filling materials, high concentration of Fe and Mn ion, mining drainage, sewage regeneration

Liping Zhang (corresponding author)

Aolei Chen

Hongbin Qu

Shouqiang Xu

Xue Zhang

Xuwen He

School of Chemical and Environmental

Engineering,

China University of Mining & Technology,

Beijing,

100083 China

E-mail: 1403561964@qq.com

## INTRODUCTION

According to the '12th five-year developing plan in coal industry',  $7.092 \times 10^9 \text{ m}^3$  of mine drainage will be discharged from all the coal mines in China in 2015, and 75% of this mine drainage will be utilized. Large quantities of mine water discharged directly may contaminate water resources and pollute the environment surrounding the mining area. Therefore, it is important to treat and reuse mine drainage to create an environment-friendly society in the mining area.

Currently, the common method for treating mine drainage is to pump it to a treatment facility above ground. The treated mine drainage is partially utilized on the ground and the rest is returned back underground as a water resource for the coal mine. This method occupies a large area, imposes expensive treatment facility costs, has a high equipment operating cost and is highly power intensive (Zhou *et al.* 2013). Underground treatment and utilization of mine water can overcome the listed shortcomings, help to maintain a balance in the natural

groundwater, save construction and operation costs and, overall, bring environmental benefits (Li *et al.* 2006, 2014). The technology for and utilization of underground disposal of mine water in underground excavating lanes are a matter of some urgency.

In recent years, there have been some reports and research about underground disposal and *in situ* reuse. Many researchers (Zhong 2001; Liu *et al.* 2003; Feng *et al.* 2004; Gu *et al.* 2007) have studied traditional water treatment technology and processes used in underground disposal; meanwhile engineering practice was developed in the Yunkuang Group and Huainan Mining Bureau. The expected treatment effect of suspended solids (SS), total dissolved solids (TDS) and turbidity was obtained; however, the goaf filling materials used in underground excavating lanes to remove these pollutants and the removal mechanism of metal ions such as Fe and Mn were not discussed.

Underground water containing Fe and Mn is widely distributed in China. In general, Fe concentration is lower than

doi: 10.2166/wst.2015.322

10 mg/L, but occasionally is between 20 and 30 mg/L. The ionic form of Fe is commonly ferrous ion, and the solubility of ferric ion is low when pH is higher than 5.0. Normally, Mn concentration is between 0.5 and 2.0 mg/L, but occasionally is between 3.0 and 5.0 mg/L (He & Li 2010). Hallberg & Johnson (2005) studied aerobic wetlands and bioreactors to remove Fe and Mn in acid mining drainage, but the removal efficiency of Mn was not perfect. Phillips *et al.* (1995) researched anaerobic ponds, aerobic ponds and bio-trickling filters to dispose of acid mining drainage, with the results showing that removal of Fe was easier than that of Mn. Li & Liu (1989), Zhang & Dai (1997), Seppane (1992), da Fonseca *et al.* (2006) and Knocke *et al.* (1991) researched and compared catalytic oxidation, contact oxidation and biological method to remove Fe and Mn, respectively, and the biological method was accepted as the best disposal method. However, this method was not scale-applied in engineering because of its disadvantages, such as long start time, unstable disposal effect and difficult automatic control.

Modified filter media are a new research area. Resende *et al.* (1999) used sulfate to activate the surface of Brazil manganese ore. The new modified manganese ore could remove different kinds of metal ions effectively. Tahir & Rauf (2004) successfully applied bentonite to remove Zn and Fe ions from flotation wastewater. Doula (2006) coated the surface of zeolite with iron oxide to remove manganese ion from drinking water. All these processing methods had a certain effect on the removal of Fe ion and Mn ion, but these methods were not used to treat groundwater or mining drainage, and there were additional costs of raw materials and modifying agents. Simultaneously, the coal gangue from the coal mining process is not handled properly either.

Therefore, the objectives of this research were: (1) to analyse the mineral composition of filling materials in mine goaf; (2) to discuss the adsorption and desorption kinetics of the goaf filling materials for removal of Fe and Mn

and analyse their removal mechanisms; and (3) to study the influencing factors on Fe and Mn removal in a simulated mine goaf.

## MATERIALS AND METHODS

### Materials

Goaf filling materials were chosen from Shendong mine goaf in Inner Mongolia, China. The goaf filling materials were composed of coal gangue, sandy soil and clay (mass ratio 45:4:1). Clay was the main adsorbing component that effectively adsorbed Fe and Mn from mining drainage. The mineral composition of the clay and the particle size distribution characteristics of the goaf are shown in Tables 1 and 2, respectively.

Table 1 shows that the clay was composed of 78.6% montmorillonite, 7.6% kaolinite, 6.4% illite and other minerals. Montmorillonite is a typical aluminium silicate mineral and has a laminar structure. Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> hydrated ions were adsorbed between the layers of montmorillonite to balance electric charges of the crystal cell, but the ion adsorption force was relatively weak. These ions could be easily replaced by other cations, like the heavier and high molecular weight metal ions and large volume organic cations.

Table 2 reveals that the goaf filling materials had a good particle size gradation, size >10 mm particle was 33.96%, size <10 mm particle was 65.6% and the constrained size particle was 11.28%. The particle size gradation showed that the goaf filling materials had a greater small size particle range to remove SS and Fe<sup>3+</sup>.

Experimental water with high turbidity and a high concentration of iron and manganese was sampled from a coal mining area. The objective was for it to meet the reuse water quality (Code for Engineering Design of Sewage Regeneration-GB503352-2002). Both qualities are listed in Table 3.

**Table 1** | Mineral composition of clay (%)

Samples	Montmorillonite	Kaolinite	Illite	Quartz	Feldspar	Calcite
1	90	3	5	2	/	/
2	74	10	8	3	/	5
3	79	10	5	3	/	3
4	70	10	8	7	5	/
5	80	5	6	3	3	3
Average	78.6	7.6	6.4	3.6	1.6	2.2

**Table 2** | Particle size distribution characteristics of goaf filling materials

Samples	Particle size distribution (%)					Constrained particle size	
	>10 mm	10–2 mm	2–0.5 mm	0.5–0.25 mm	<0.25 mm	d <sub>60</sub> (mm)	d <sub>30</sub> (mm)
1	20	47	22	7	4	5.4	1.142
2	47	19	18	10	6	14.3	1.52
3	46	31	12	5	6	13.5	3.4
4	19.7	44	23.7	7.3	5.3	4.42	1.45
5	37.1	27.8	20.9	6.6	5.4	9.6	1.68
Average	33.96	33.76	19.32	7.18	5.34	9.444	1.838

**Table 3** | Experimental water and reuse water quality

Items	pH	Turbidity (NTU)	Fe (mg/L)	Mn (mg/L)
Experimental water	7.05	301.5	10.08	2.14
Reuse water	6.0 ~ 9.0	<5	<0.3	<0.2

The simulated goaf seepage equipment (1.7 m × 0.3 m × 0.3 m) was made of Plexiglass, and was filled with goaf materials. The two ends of the equipment had inlet and outlet ports, and there were two sampling holes, 0.5 m and 1.0 m away from the inlet, on the bottom of one side of the equipment. A schematic diagram of this equipment is shown in Figure 1.

## General procedure

### Sequencing batch isotherm adsorption experiments of goaf filling material

Goaf filling material was quantified at 40 g and put into a 250 mL iodine flask. This was followed by adding 200 mL solution prepared by mixing FeSO<sub>4</sub> (concentration 1 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 40 mg/L, respectively) and MnCl<sub>2</sub> (concentration 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L, respectively). The flasks were placed in an air oscillator at constant temperature and shaken under the

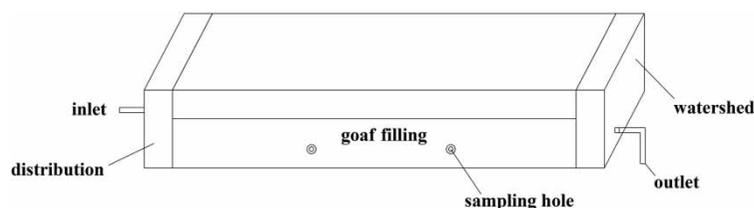
experimental conditions of 25 ± 1 °C, 100 r/min, for 8 hours. Samples were taken at different time points, and were analysed for total iron and Mn<sup>2+</sup> concentrations.

### Desorption experiments of saturated goaf filling materials

Forty grams of adsorption-saturated goaf filling materials were put into a 250 mL iodine flask. Two hundred millilitres of desorption solution (CaCl<sub>2</sub> concentration 0.01 mol/L) was then added to the flasks. The flasks were then placed in an air oscillator for 8 hours at constant temperature and shaken under the experimental conditions of 25 ± 1 °C, 100 r/min. The samples were taken and analysed for total iron and Mn<sup>2+</sup> concentrations.

### Experiments of hydraulic loading, pollutant concentration and pH effect on goaf filling material

The experimental water was pumped to the inlet of the simulated goaf experimental equipment with a flow of 0.6 L/min, 1.2 L/min and 2.4 L/min, respectively, to determine an optimum flow. The inlet concentrations of Fe and Mn (Fe 20 mg/L, Mn 2 mg/L; Fe 40 mg/L, Mn 2 mg/L; Fe 10 mg/L, Mn 4 mg/L) were used and the right concentration was obtained. Finally, the pH was adjusted with HCl and NaOH to 3.5, 7 and 10.5, respectively.

**Figure 1** | Diagram of simulated goaf experimental equipment.

## Detection method

The mineral compositions of goaf filling materials were determined by X-ray diffraction (D8 ADVANCE). The pH of the solution was determined with a pH meter (HI98128). Turbidity was tested with spectrophotometry (GDS-3). Total iron was determined with the phenanthroline spectrophotometry method (Unico 2100). Manganese was tested with formaldehyde oxime spectrophotometry (Unico 2100).

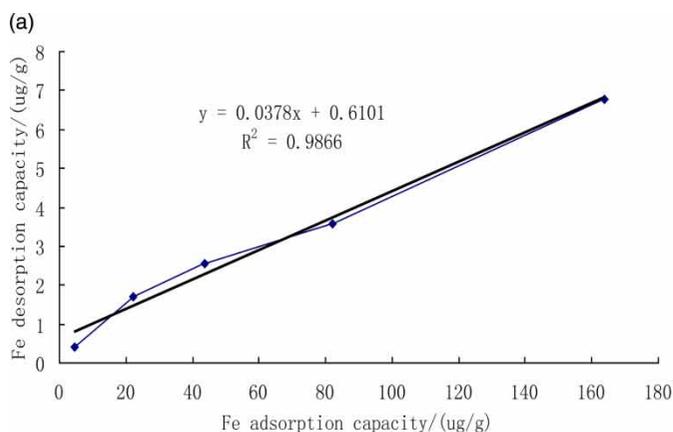
## RESULTS AND DISCUSSION

### Fe and Mn adsorption and desorption kinetics of goaf filling materials

The desorption process of Fe and Mn on goaf filling materials is closely related to their adsorption behaviour.

**Table 4** | Adsorption and desorption of Fe and Mn on goaf filling materials

Fe concentration (mg/L)	1	5	10	20	40
Fe adsorption capacity ( $\mu\text{g/g}$ )	4.432	21.04	39.75	78.17	163.79
Fe desorption capacity ( $\mu\text{g/g}$ )	0.398	1.71	2.54	3.586	6.765
Fe desorption ratio (%)	8.98	8.13	6.39	4.59	4.13
Mn concentration (mg/L)	1	2	3	4	5
Mn adsorption capacity ( $\mu\text{g/g}$ )	3.25	6.4	9.5	12.5	15.25
Mn desorption capacity ( $\mu\text{g/g}$ )	0.298	0.67	0.92	1.38	1.52
Mn desorption ratio (%)	9.17	10.47	9.68	11.04	9.97



$\text{CaCl}_2$  was used as the desorption agent. The results of the kinetic study on goaf filling materials are shown in Table 4 and Figures 2(a) and 2(b).

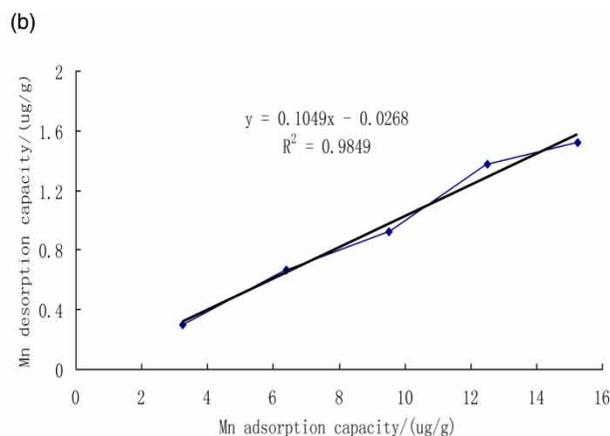
Figure 2 shows that both Fe and Mn desorption on goaf filling materials fitted the linear model very well and the desorption capacity of Fe and Mn on goaf filling materials increased with the rise in adsorption capacity of Fe and Mn, respectively. The Fe desorption equation was  $y = 0.0378x + 0.6101$ ,  $R^2 = 0.9866$ , reaction rate constant for Fe ( $k_d(\text{Fe}) = 0.0378 \text{ mL/g}$ ). The Mn desorption equation was  $y = 0.1049x - 0.0268$ ,  $R^2 = 0.9849$ ,  $k_d(\text{Mn}) = 0.1049 \text{ mL/g}$ .

Under laboratory conditions, the maximum desorption capacity of Fe on goaf filling materials was  $6.765 \mu\text{g/g}$  and the maximum desorption ratio was 8.98%. The maximum desorption capacity of Mn on goaf filling materials was  $1.52 \mu\text{g/g}$  and the maximum desorption ratio was 11.04%. Therefore, goaf filling materials could be a good substrate choice to remove Fe and Mn due to the low desorption capacity and desorption ratio but high adsorption capacity.

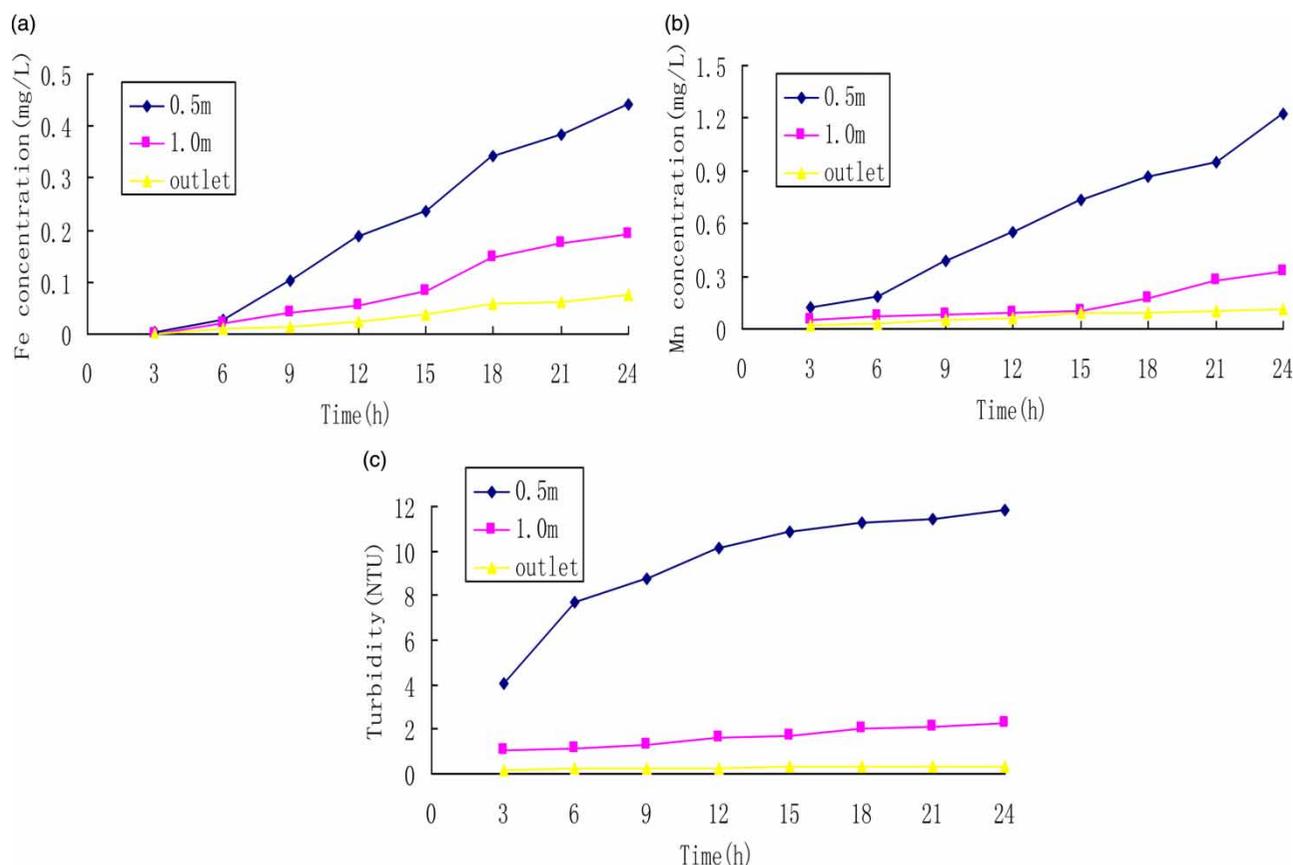
### Removal experiments of Fe and Mn on goaf filling materials

The experimental water was pumped through the inlet of the simulated goaf experimental equipment. The quality of experimental water was Fe  $10.08 \text{ mg/L}$ , Mn  $2.14 \text{ mg/L}$  and turbidity  $301.5 \text{ NTU}$  (nephelometric turbidity units). The water flow was  $1.2 \text{ L/min}$ . Samples were taken from the outlet and the two sampling holes, which were  $0.5 \text{ m}$  and  $1.0 \text{ m}$  from the inlet, respectively. The results are displayed in Figures 3(a)–3(c).

It is clearly seen from Figure 3(a) that the Fe removal efficiency of goaf filling materials was noticeable. In the continuous adsorption experiments, Fe concentration



**Figure 2** | The relationship between adsorption and desorption of Fe and Mn on goaf filling materials.



**Figure 3** | Fe, Mn and turbidity removal on goaf filling materials.

increased over time as measured at the three sampling holes, but was still lower than 0.5 mg/L. On further increase in inlet Fe loading, removal efficiency gradually decreased. Figure 3(b) shows that Mn had a similar concentration change trend as Fe, but the Mn removal efficiency was lower than Fe. After 24 hours of continuous treatment, Mn concentration reached 1.227 mg/L on the 0.5 m sampling hole, which indicated the lower adsorption capacity of Mn on goaf filling materials. High turbidity removal efficiency could be obtained, as shown in Figure 3(c). As the inlet concentrations increased, the effluent turbidity also increased gradually.

### Effect of inlet hydraulic loading

The effect of hydraulic loading was also analysed by adjusting the inlet flow rate. The samples were taken from the outlet. Experimental results are shown in Figures 4(a)–4(c).

Figure 4 indicates that the hydraulic loading could affect the removal efficiency of Fe, Mn and turbidity using goaf filling materials. The increased hydraulic loading led to an increase in effluent concentration of Fe, Mn and turbidity. After 24

hours of continuous treatment, when the inlet flow rate was 2.4 L/min, Mn could not meet the required standards of the Code for Engineering Design of Sewage Regeneration-GB503352-2002. It also indicated that the removal efficiency did not vary much from 0.6 L/min to 1.2 L/min.

### Effect of inlet contaminant concentration

For this, the quality of experimental water was changed; the water flow was 1.2 L/min. The samples were taken from the outlet. Experimental results are shown in Figures 5(a) and 5(b).

As seen in Figure 5(a), an increase in inlet Fe concentrations had some effect on outlet Fe concentration. When the inlet Fe concentration was 40 mg/L, the highest outlet concentration of Fe was 0.153 mg/L, which was much lower than the reuse requirement (0.3 mg/L). Meanwhile, the removal efficiency (99.62%) was higher than that of inlet Fe concentration (10 mg/L). Figure 5(b) also shows that higher inlet Mn concentration could affect the outlet concentration. When the inlet Mn concentration was 4 mg/L, the highest outlet concentration of Fe was 0.257 mg/L, which was

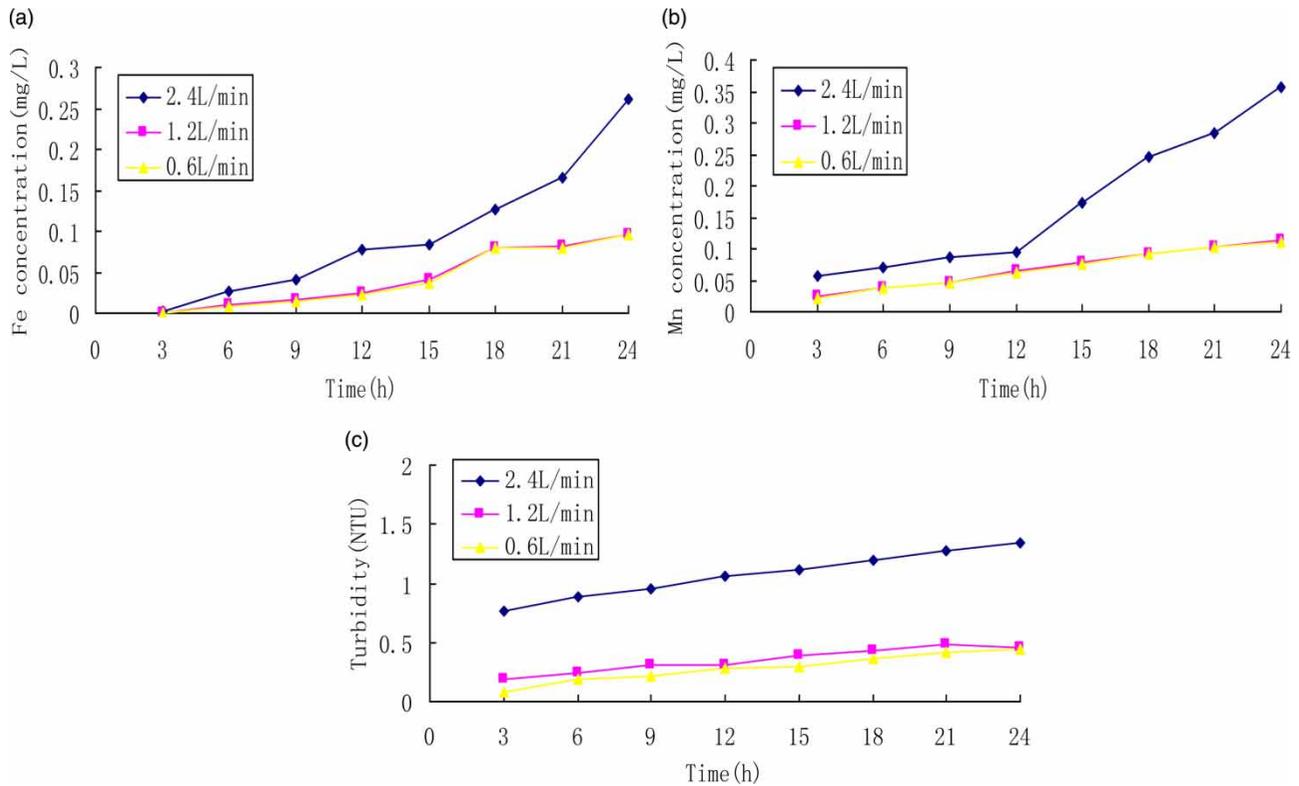


Figure 4 | Hydraulic loading effect on goaf filling materials.

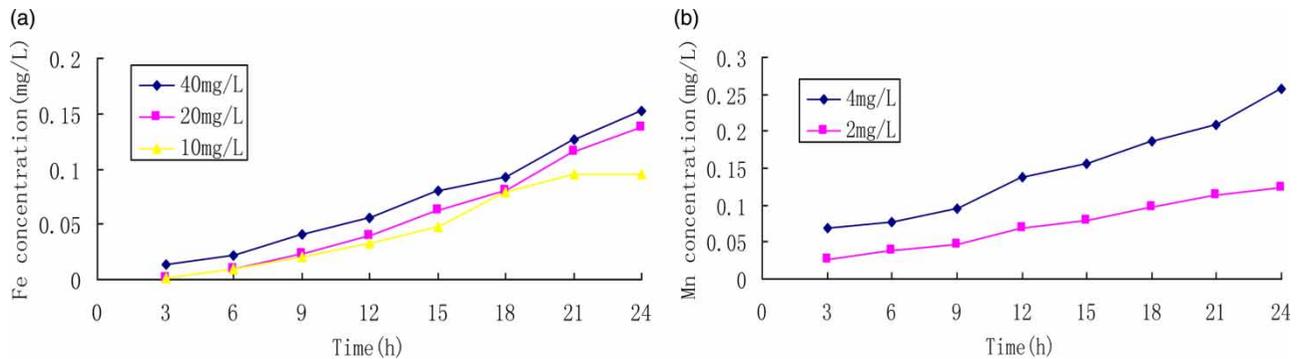


Figure 5 | Contaminant concentration effect on goaf filling materials.

higher than the reuse requirement (0.2 mg/L). However, it is worthwhile noting that during the short experimental period, an increase in pollution load of Fe and Mn could not induce an apparent effect on removal efficiency, but could shorten the adsorption saturation time of goaf filling materials.

#### Effect of inlet pH value

The quality of experimental water was Fe 10.08 mg/L, Mn 2.14 mg/L, turbidity 301.5 NTU, but the pH was adjusted

with HCl and NaOH to 3.5, 7 and 10.5, respectively. The flow rate was 1.2 L/min. Samples were taken from the outlet. The results are displayed in Figures 6(a) and 6(b).

As seen in Figure 6(a), in acidic condition, the effluent concentration of Fe increased rapidly during the experimental period; the highest Fe concentration reached 0.793 mg/L, which could not be reused. In alkaline condition, the removal efficiency of Fe was the highest; the effluent concentration was only 0.105 mg/L which was much lower than the reuse requirement (0.3 mg/L). Figure 6(b) shows that in acidic

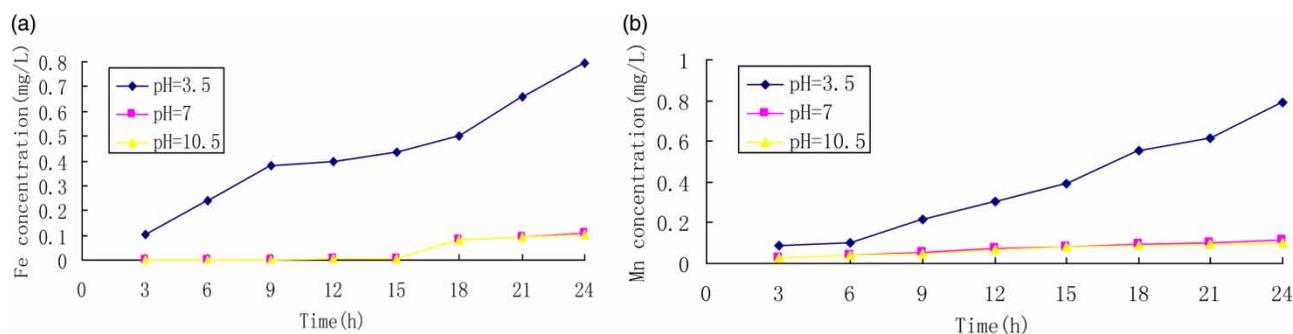


Figure 6 | pH effect on goaf filling materials.

experimental condition, within the first 6 hours, the effluent concentration of Mn was lower than 0.2 mg/L, but the concentration increased significantly thereafter. The highest effluent concentration of Mn was 0.792 mg/L. Therefore, goaf filling materials were not able to remove Fe and Mn effectively in acidic experimental condition; however, a stable treatment effect in neutral and alkaline condition with goaf filling materials could be obtained.

## REAL APPLICATION IN SHENHUA COAL GROUP

The Shendong coal mine (Shenhua Coal Group) in China is an important coal base for export, which has a 10 million ton class capacity. The real application using an underground excavating lane to treat mining drainage was 100 m<sup>3</sup>/h, the scale of the goaf was about 400 m in length, 5 m in width and 4 m high. Using two pumps to lift mining drainage to the goaf, the inlet flow was 3 m/h. The mining drainage went through the goaf filled with materials such as gangue, soil and clay. In order to guarantee that the effluent achieved reuse water quality for the hydraulic pressure stanchion, a complex sedimentation tank, discal filter and Fe-Mn filter were used after the goaf process. The mining drainage and reuse water quality are listed in Table 5.

Table 5 shows that the goaf combined with sedimentation tank and filters could remove SS, turbidity, Fe and Mn

effectively, and the effluent quality could meet the demand of the hydraulic pressure stanchion. This goaf treatment system has worked for more than 5 years, and the monitoring results show that the goaf still has a good removal effect on SS, turbidity, Fe and Mn. It can reduce the pollution loading and provide a powerful buffer capacity for the following treatment processes. After the goaf filling materials have exceeded the saturated capacity, they should be cleaned through water backwashing and pickling technology. The electric power consumption of two pumps (motor current 15 kW each) is the main treatment cost, and there were no chemical agent and labour costs for the full automatic control. According to the real-application project that has been operating for more than 5 years, the average cost per ton of mining drainage is about 0.55 RMB. The price of industrial water in mining areas is about 3.56 RMB per ton, thus using the goaf filling materials to treat mining drainage could bring considerable economic benefit.

## CONCLUSIONS

The conclusions are as follows:

- (1) The goaf filling materials composed of coal gangue, sandy soil and clay (mass ratio 45:4:1) could effectively remove Fe and Mn from mining drainage.
- (2) The isothermal adsorption equations of Fe and Mn ions met the linear model.

Table 5 | Mining drainage and reuse water quality

Items	pH	Turbidity (NTU)	SS (mg/L)	Total Fe concentration (mg/L)	Mn concentration (mg/L)	Total hardness (CaCO <sub>3</sub> ) (mg/L)	TDS (mg/L)
Mining drainage	7.17	98.6	1006.6	6.8	0.69	322.6	618
Reuse water	7.56	1.2	4.2	0.16	0.096	230	336
Reuse standard	6–9	5	10	0.3	0.2	450	1,000

- (3) Goaf filling materials could be a good substrate choice to remove Fe and Mn due to low desorption capacity (Fe 6.765 µg/g, Mn 1.52 µg/g) and desorption ratio (Fe 8.98%, Mn 11.04%) but high adsorption capacity (Fe 163.79 µg/g, Mn 15.25 µg/g).
- (4) During the experimental period, Fe and Mn from mining drainage could be removed stably in the condition of flow rate 1.2 L/min, Fe concentration less than 40 mg/L, Mn concentration less than 2 mg/L and pH in the neutral or alkaline range.
- (5) The real-application project using goaf filling materials to treat mining drainage in Shendong coal mine showed that the average cost per ton of mining drainage was about 0.55 RMB, which could bring considerable economic benefit for the coal mining enterprise.

## ACKNOWLEDGEMENT

This paper was supported by the National High Technology Research and Development Program of China (2008AA06Z305).

## REFERENCES

- da Fonseca, M. G., de Oliveira, M. M. & Arakaki, L. N. H. 2006 Removal of cadmium, zinc, manganese and chromium cations from aqueous solution by a clay mineral. *J. Hazard. Mater.* **137** (1), 288–292.
- Doula, M. K. 2006 Removal of Mn<sup>2+</sup> ions from drinking water by using clinoptilolite and a clinoptilolite-Fe oxide system. *Water Res.* **40** (1), 3167–3176.
- Feng, L. L., Zhu, Y. L., Chen, S. Z. & Shan, A. Q. 2004 Research of results on disposal of mine drainage containing suspended solids through goaf. *Energy Environ. Protect.* **18** (6), 40–42.
- Gu, Y. X., Zhou, Z. N. & Li, Y. M. 2007 Research on resource utilization of mine water in goaf. *Coal Sci. Technol.* **35** (4), 90–92.
- Hallberg, K. B. & Johnson, D. B. 2005 Biological removal from acid mine drainage in constructed wetlands and prototype bioreactors. *Sci. Total Environ.* **33** (8), 115–124.
- He, X. W. & Li, F. Q. 2010 New technology and development tendency of mine water treatment. *Coal Sci. Technol.* **38** (11), 17–22.
- Knocke, W. R., Occiano, S. C. & Hungate, R. 1991 Removal of soluble manganese by oxide-coated filter media: sorption rate and removal mechanism issues. *J. AWWA* **91** (8), 64–69.
- Li, K. B. & Liu, C. 1989 *Remove Fe and Mn from Underground Water*. China Architecture Industry Publishing, Beijing.
- Li, F. Q., Yang, J., He, X. W., Tang, Y. G., Yang, J. P. & Tian, T. 2006 Study of the reclamation and reuse of mine water with high TDS, iron and manganese content. *J. China Univ. Mining Technol.* **33** (5), 637–641.
- Li, F. Q., He, X. W., Lv, X. L., Yang, J. P. & Tian, T. 2014 Engineering application and new technology of underground mine water treatment. *Coal Sci. Technol.* **42** (1), 117–120.
- Liu, L. M., Lian, C. J. & Wei, J. Q. 2003 Underground mine water disposal method and water supply system. *Coal Eng.* **9** (2), 58–60.
- Phillips, P., Bender, J., Simms, R., Rodriguez, S. & Britt, C. 1995 Manganese removal from acid coal-mine drainage by a pond containing green algae and microbial mat. *Water Sci. Technol.* **31** (12), 161–170.
- Resende, P. C., Barrado, F. S. & Martins, A. H. 1999 Sulfuric activation of a Brazilian manganese ore for heavy metals removal. *Hydrometallurgy* **51** (1), 325–333.
- Seppane, H. T. 1992 Experience of biological iron and manganese removal in Finland. *J. IWEM* **6** (2), 333–341.
- Tahir, S. S. & Rauf, N. 2004 Removal of Fe(II) from the wastewater of a galvanized pipe manufacturing industry by adsorption onto betonies clay. *J. Environ. Manage.* **73** (1), 285–292.
- Zhang, J. & Dai, Z. S. 1997 Principle and application of Mn removal with strong oxidant. *Water Wastewater Eng.* **22** (3), 16–18.
- Zhong, Y. M. 2001 Underground treatment of coal mining drainage. *Indust. Water Wastewater* **32** (4), 27–28.
- Zhou, R. L., Gao, L., Guo, Z. Q., Cui, D. F. & Yang, J. C. 2013 Underground direct treatment and recycle of coal mine water. *China Water Wastewater* **29** (4), 71–79.

First received 29 October 2014; accepted in revised form 9 June 2015. Available online 8 August 2015