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Chromium (VI) reduction in aqueous solutions using coal gangue

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ABSTRACT

Coal gangue can be applied to remove chromium (VI) from wastewater because it exhibits excellent reduction ability. Cr(VI) could be almost completely reduced to the lower toxicity form, Cr(III). Coal gangue before and after treatment was characterised by X-ray diffraction, SEM, EDS and FT-IR spectrums. The main active materials in coal gangue were siderite and pyrite. Dynamic experiments with different initial concentrations of Cr(VI) demonstrated that the reduction of Cr(VI) showed zero-order kinetics. The zero-order plots of c vs. t represented ideal linearity and regression coefficients were above 0.938. The treatment capacity calculated from the kinetics model was in good agreement with the experimental data, both of which were greater than 18.5 mg/g. The reduction of Cr(VI) by coal gangue was strongly pH-dependent. In fact, both the decomposition of siderite and pyrite and the reduction of Cr(VI) hardly occurred without the presence of H^+. Under the optimum conditions, removal of Cr(VI) by coal gangue was effective and economical. The concentration of hexavalent chromium in the treatment water was lower than 0.05 mg/L, and the total chromium was far below the emission standard of 1.5 mg/L.

Keywords: Coal gangue; Cr(VI); Reduction; Kinetics model; Mechanism

1. Introduction

Hexavalent chromium [Cr(VI)] is one of the most toxic, carcinogenic metals [1–6], and is a pollutant due to the improper discharge of chromium-related industries such as electroplating, tanning and anti-corrosion protection [7–10]. A large amount of Chromium (VI) wastewater discharge would cause serious environmental pollution. More researches have turned to study of removing Cr(VI) from wastewater since human beings realize the harm of Cr(VI) [11–14]. Convenient and low-cost methods are important for large-scale Cr(VI) wastewater treatment, so waste materials [15–17] have been applied to remove Cr(VI), including: used tires and sawdust [18]; activated carbon derived from agricultural waste materials [19]; fly ash [20]; waste shot-blast fines recovered from surface finishing operations in cast-iron foundry [21]; sulphuric acid-modified avocado seed [22]; and humic substances [23]. The methods mentioned above can be divided into adsorption and reduction [24]. Cr(VI) in a liquid can be enriched and immobilised by adsorption [25], which is convenient for further treatment. The second method of Cr(VI) wastewater decontamination is by the reduction of Cr(VI) to Cr(III) followed by chemical precipitation [6]. Cr(III) is relatively nontoxic [26,27]. The latter method could be a convenient and economical way to remove Cr(VI) from wastewater if an effective and low-cost reductant can be found.

Coal gangue is a waste material produced during coal mining [28]. It accounts for 15–20% of the output of raw coal and is one of the largest industrial solid wastes worldwide. The chemical composition of coal gangue from different areas varies. Most coal gangue is rich in carbon, aluminium, silicon, calcium and iron. According to its composition, coal gangue is generally used to generate electricity, produce cement, or as a building material. However, the research of coal gangue as a reductant to remove Cr(VI) has rarely been reported to date.

Here, we show that some coal gangue exhibits excellent reduction ability. The conditions for reduction of Cr(VI) to Cr(III) by coal gangue were studied, and the kinetic properties, as well as the mechanisms of reduction are also discussed.

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2. Experimental

2.1. Materials and instruments

Potassium dichromate, diphenyl carbazide (DPC) and all other reagents used in the study were of analytical grade. Coal gangue was obtained from Xinjiang Zhundong colliery. It was smashed and ground to 100 meshes. The main chemical components are listed in Table 1.

The pH of the solutions was determined using a PHS-3B meter (Leici, China). The concentration of Cr(VI) was measured using a 7230G spectrophotometer (Shanghai, China) at 540 nm. Some trace elements in the solutions were quantified using inductively coupled plasma optical emission spectroscopy (Vista-pro CCD Simultaneous ICP-OES, Varian, USA). To investigate the changes in the micro-composition, samples before and after reduction were recorded on a D8 ADVANCE Powder X-ray Diffractometer (XRD; Bruker, Germany), an AVATAR FT-IR spectrometer (Nicolet, USA), a SUPRA55VP Scanning Electron Microscope (SEM; Zeissm, Germany) and a PHI-5300 Electronic Differential System (EDS; ULVCA-PHI, USA).

2.2. Reduction of Cr(VI)

A 1000 mg/L stock solution of Cr(VI) was prepared by dissolving the required amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water. The stock solution was diluted to obtain different concentration of Cr(VI) solutions from 40 to 100 mg/L.

The experiments were performed in 250 mL conical flasks by mixing coal gangue with Cr(VI) solution. The mixtures were stirred at 120 rpm for a certain time and then were centrifuged at 5000 rpm for 10 min. Cr(VI) in the supernatant (marked A) was detected using a spectrophotometer.

2.3. Precipitation of Cr(III)

Diluted ammonia and flocculant were added into supernatant A to regulate acidity and to precipitate the Cr(III). After stirring for 10 min, the sludge was separated from the solution by centrifuging at 5000 rpm for 10 min. The residual Cr(VI), total Cr and other trace elements in the solution were determined using a spectrophotometer and ICP-OES, respectively.

Table 1
The chemical components of coal gangue (mass%)

Component	Coal gangue
SiO_2	47.40
Al_2O_3	13.25
Fe_2O_3	9.91
MgO	1.63
CaO	1.79
SO_3	2.07
TiO_2	1.65
Loss	21.93

2.4. Determination of the Cr(VI) concentration

At the end of the each experiment, 25 mL of supernatant was put into a 50 mL volumetric flask with 2 mL DPC. Five minutes later, 0.5 mL H_2SO_4 and 0.5 mL H_3PO_4 were put into the flask mentioned above, and then distilled water was added to the scale. 15 min later, the concentration of Cr(VI) was determined using a spectrophotometer at 540 nm (method GB7466-87).

3. Results and discussions

3.1. Reaction properties

3.1.1. The influence of pH on Cr(VI) reduction

The results shown in Fig. 1 indicate that the process of Cr(VI) reduction is strongly pH-dependent [29,30]. In mildly acidic solutions (pH above 5), coal gangue scarcely reacted with Cr(VI) whereas in a strong acidic solution, especially when the pH was below 4, the influence became obvious. Furthermore, the lower the pH in the system the easier the reaction was. The details of how the pH effects the reduction will be discussed later.

3.1.2. The influence of the amount of coal gangue on Cr(VI) reduction

Cr(VI) reduction in the system was related to the content of coal gangue. The concentration of Cr(VI) decreased with the increasing amount of coal gangue over the same time. Fig. 2 shows that the reaction could be accomplished in 90 min when the amount of coal was more than 0.5 g. Finally, there was only 0.036 mg/L Cr(VI) left in the solution.

3.1.3. The influence of the stirring rate on Cr(VI) reduction

Under the same experimental conditions, the effect of the stirring rate was not significant (Fig. 3). When the stirring

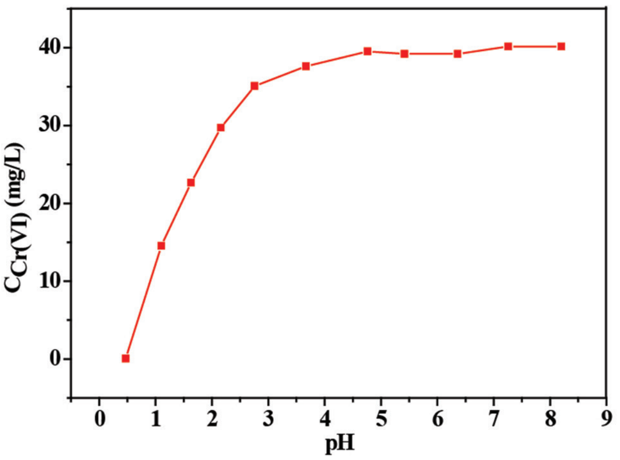


Fig. 1. The effect of pH on the reduction of Cr(VI). Initial concentration of Cr(VI): 40 mg/L; volume: 100 mL; amount of coal gangue: 0.5000 g; time: 120 min; stirring rate: 120 rpm.

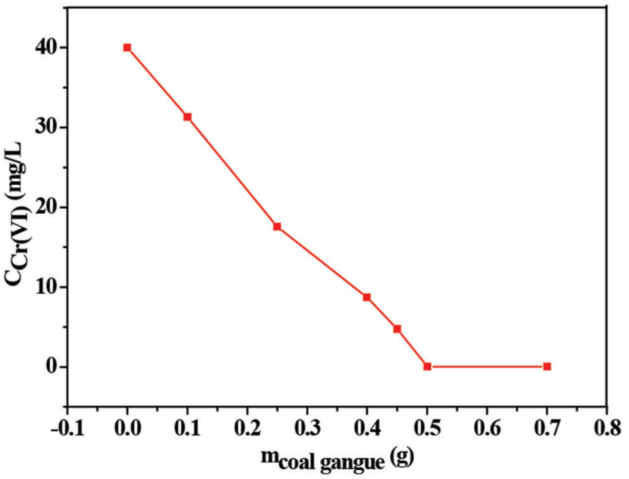


Fig. 2. The effect of the amount of coal gangue on Cr(VI) reduction. Initial concentration of Cr(VI): 40 mg/L; volume: 50 mL; time: 90 min; stirring rate: 120 rpm, pH: 1.00.

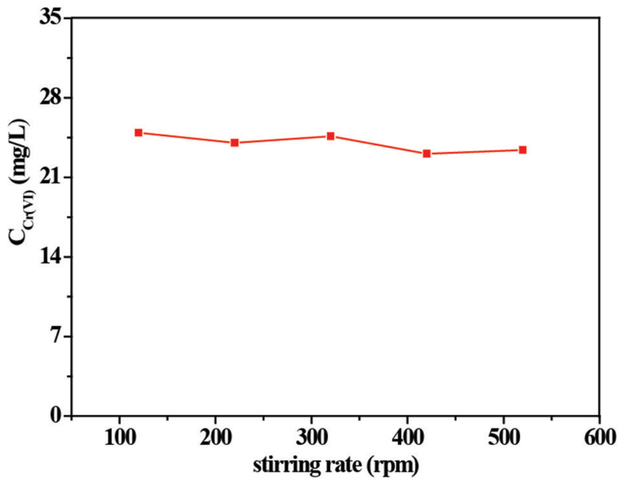


Fig. 3. The effect of stirring rate on Cr(VI) reduction. Initial concentration of Cr(VI): 40 mg/L; volume: 50 mL; time: 30 min; the amount of coal gangue: 0.2500 g; pH: 1.00.

rate was increased from 100 to 600 rpm, the equilibrium concentration of Cr(VI) did not change.

3.1.4. The influence of time on Cr(VI) reduction

In this part, experiments were carried out to determine the influence of time on the reduction of Cr(VI) and the effect of stirring on the reaction rate. We designed five experiments marked I, II, III, IV, and V. Experiments I to IV were performed by stirring at 120 rpm for 210 min, then keeping still, and the initial concentration of Cr(VI) ranged from 40 to 100 mg/L. In experiment V, there was no stirring. The initial concentration of Cr(VI) used in experiment V was 100 mg/L, which is the same as that in experiment IV. Fig. 4 shows that the concentration of Cr(VI) decreased with increasing reaction time. We also found that the concentration of Cr(VI) during stirring decreased more rapidly than that without stirring. The fitting curves of I to IV obtained during stirring, like that of without stirring tended to be parallel. The results indicate that the reaction rate was not dependent upon the initial concentration of Cr(VI), which fits the zero-order reaction kinetics expressed by the following equations [31,32].

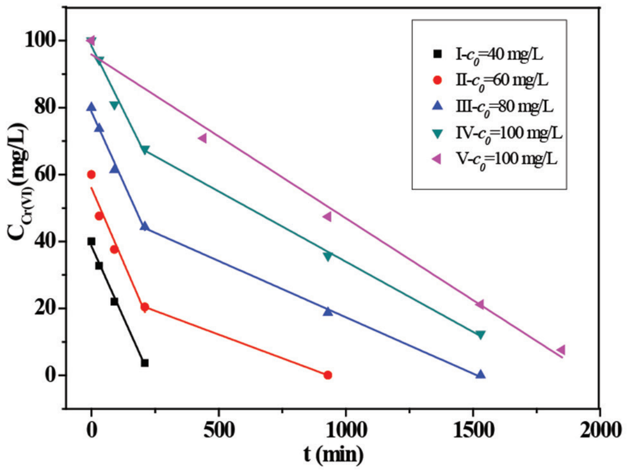


Fig. 4. The effect of time and initial concentration on Cr(VI) reduction. Volume: 100 mL; amount of coal gangue: 0.5000 g; stirring rate: 120 rpm; stirring time: 210 min; pH: 1.00; temperature: 323 K.

$$v = -\frac{dc}{dt} = kc^0 = k \tag{1}$$

$$dc = -kdt \tag{2}$$

$$\int_{c_0}^{c} dc = -k\int_{0}^{t} dt \tag{3}$$

$$c - c_0 = -kt \tag{4}$$

where v is the reaction rate of Cr(VI) (mg/L·min); k is the rate constant (mg/L·min); t is the reaction time (min); c_0 is the initial concentration of Cr(VI) (mg/L); c is the concentration of Cr(VI) after a certain reaction time (mg/L).

The correlation parameters from the fitting curves are presented in Table 2, from which we can find that the rate constants were similar under the same conditions and that the initial concentrations c_0 agree well with the given concentration (c_g) in the experiment. The zero-order plots of c vs. t represent linearity and all of the regression coefficients are above 0.939.

Experiment I and V were performed with and without stirring, respectively. However experiments II–IV involved two processes. The kinetics equations of reduction of Cr(VI) with stirring and without stirring could express according to experiment I and V as follows:

Kinetics equation with stirring:

$$c - c_0 = -0.169t \tag{5}$$

Table 2
Kinetic parameters for reduction of Cr(VI) at 323 K

Experiment	k			R^2		
	Stirring	Without stirring	c_0 (mg/L)	c_g (mg/L)	Stirring	Without stirring
I	0.169	-	38.58	40	0.990	–
II	0.176	0.023	56.00	60	0.939	100
III	0.168	0.033	78.71	80	0.984	0.997
IV	0.153	0.042	98.34	100	0.956	0.997
V	-	0.048	95.86	100	-	0.989

Kinetics equation without stirring:

$$c - c_0 = -0.048t \tag{6}$$

Obviously, the reaction of Cr(VI) with coal gangue proceeded more quickly with stirring than that without, which is attributed to the fact that the stirring accelerated the mass transfer.

3.2. Experiment results

After treatment under the optimum experimental conditions, coal gangue separated by centrifuging was put into distilled water at pH 1 for 24 h, and the Cr dissolved in the supernatant was detected by ICP. The concentration of Cr was lower than 0.05 mg/L. Ammonia and flocculating agent were added into the wastewater to precipitate Cr(III) and other possible elements released from coal gangue after reduction. We observed green and brown floccules appearing successively during the addition of ammonia.

To determine whether the water after precipitation met the emission standard, the concentration of total Cr, Cr(VI), and other toxic elements were measured (Table 3). The total Cr and Cr(VI) were 0.17 mg/L and 0.036 mg/L respectively, which is lower than the emission standard (GB8978-1996) of 1.5 mg/L and 0.5 mg/L. Toxic elements and heavy metals also met the demands of the emission standard.

3.3. The mechanism of the Cr(VI) removal by coal gangue

Coal gangue before and after treatment was analysed using a FT-IR spectrometer (Fig. 5). According to the characteristic peak, some main groups can be observed in both samples, including: free OH groups at 3696 cm^{-1} and 3622 cm^{-1}; aliphatic C-H stretching at 2924 cm^{-1} and 2854 cm^{-1}; Si-O stretching vibration at 1300 cm^{-1} to 800 cm^{-1} [33,34]. However, the peak at 1434 cm^{-1}, which was attributed to a CO_3^{2-} group disappeared in spectrum 2. The difference between spectrums 1 and 2 indicates that there were some carbonates in the coal gangue that were consumed during the reduction of Cr(VI).

Table 3
The concentrations of elements in water after removal of Cr(VI) (mg/L)

Concentration element	c_{As}	c_{Cd}	c_{Cu}	c_{Ni}	c_{Cr}	$c_{Cr(VI)}$
GB8978-1996	<0.5	<0.1	<1	<1	<1.5	0.5
Treated water	0.02	<0.01	<0.01	<0.01	0.17	0.036

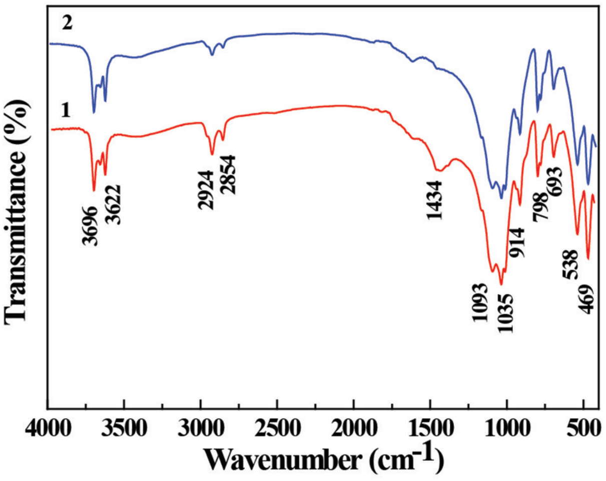


Fig. 5. FT-IR spectrums of coal gangue (1: before reduction; 2: after reduction).

The X-ray results (Fig. 6) indicate that the main substances of the coal gangue were quartz (SiO_2), kaolinite 1A ($Al_2Si_2O_5(OH)_4$), siderite ($FeCO_3$), pyrite (FeS_2) and dolomite ($CaMg(CO_3)_2$). After mixing with the solution of Cr(VI) for 6 h, the peaks of siderite, pyrite and dolomite disappeared.

SEM and EDS (Fig. 7) show that the sample before reduction was different from to that after reduction. The main elements in the former were C, O, Si, Mg, Al and Fe, and the later consisted of C, O, Si and Al. The SEM images show that the coal gangue before treatment represented three-dimensional structure with a greater porosity. However in coal gangue after reduction, the layer structure is similar to that in clay mineral.

According to the FT-IR spectrums, XRD, SEM and EDS, the main active substances in coal gangue can be inferred. Both siderite and pyrite participated in the reduction of Cr(VI). The whole reaction can be divided into two processes: releasing Fe^{2+} and S_2^{2-} from coal gangue and then reducing Cr(VI). The former was controlled by the acidity of the solution because siderite and pyrite can decompose in an acidity solution. Furthermore, the stronger the acid

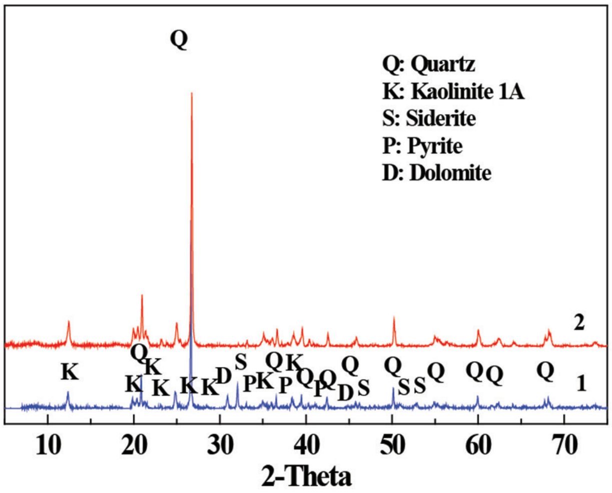


Fig. 6. X-ray diffraction patterns of coal gangue (1: before reduction; 2: after reduction).

was, the faster the reaction became. S_2^{2-} is very unstable in acid solution, it will rapidly be resolved into sulphur and hydrogen sulphide. The process of release of Fe^{2+}, S and H_2S can be described as in Eqs. (7)–(9) [35,36].

$$FeCO_3 + H^+ \rightarrow Fe^{2+} + CO_2 \uparrow + H_2O \tag{7}$$

$$FeS_2 \rightarrow Fe^{2+} + S_2^{2-} \tag{8}$$

$$S_2^{2-} + H^+ \rightarrow S + H_2S \tag{9}$$

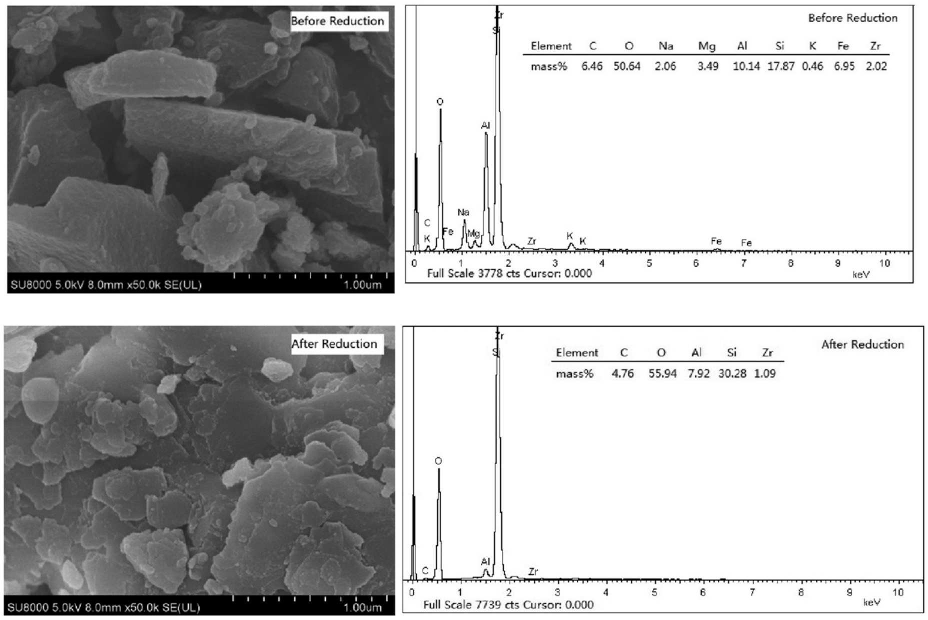
Although, there were many substances in the system (containing Mg^{2+}, Ca^{2+} from dolomite, and so on), but only those of standard potential was lower than 1.36 V can be oxidized by Cr(VI) ($\varphi^\theta(Cr_2O_7^{2-}/Cr^{3+}) = 1.36V$). Therefore, Fe^{2+} ($\varphi^\theta(Fe^{3+}/Fe^{2+}) = 0.77V$), S($\varphi^\theta(S_2O_3^{2-}/S) = 0.5V$), $\varphi^\theta(S_4O_6^{2-}/S_2O_3^{2-}) = 0.08V$, $\varphi^\theta(H_2SO_3/S_4O_6^{2-}) = 0.507V$, $S_2O_6^{2-}/S_4O_6^{2-}) = 0.569V$, $\varphi^\theta(SO_4^{2-}/S_4O_6^{2-}) = -0.25V$), and H_2S ($\varphi^\theta(S/H_2S) = 0.144V$) could take part in a redox reaction. The oxidation-reduction of sulphur and hydrogen sulphide with Cr(VI) was complex as shown by the variability in the oxidation state of sulphide. However, in fact, all the oxidation states will eventually be oxidized to SO_4^{2-} (a stable state) if the content of Cr(VI) is sufficient [37,38]. It was difficult to directly test whether all the oxidation states of sulphide had been transformed into SO_4^{2-}, but we can infer indirectly that they were based on the facts below. First, all the electrode potentials in the acidity solution [except $\varphi^\theta(S_2O_8^{2-}/SO_4^{2-}) = 1.96V$ and $\varphi^\theta(S_2O_8^{2-}/H_SO_4^{2-}) = 2.08V$] were lower than 1.36 V, which means the oxidation states of sulphide could be oxidized by Cr(VI). Second, the fact that ferrous was oxidized to ferric (brown floccules can be observed when ammonia was added into the system) demonstrated all the oxidation sates of sulfide could be oxidized into SO_4^{2-} according to the rule reductant with low electrode potential prior to high electrode potential can be oxidized [electrode potential of $\varphi^\theta(Fe^{3+}/Fe^{2+})$ is higher than that of $\varphi^\theta(S_2O_3^{2-}/S)$, $\varphi^\theta(S_4O_6^{2-}/S_2O_3^{2-})$, $\varphi^\theta(H_2SO_3/S_4O_6^{2-})$, $\varphi^\theta(S_2O_6^{2-}/S_4O_6^{2-})$, and $\varphi^\theta(SO_4^{2-}/S_4O_6^{2-})$]. The main reaction can be described as follows:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \tag{10}$$

$$Cr_2O_7^{2-} + S + 6H^+ \rightarrow 2Cr^{3+} + SO_4^{2-} + 3H_2O \tag{11}$$

$$4Cr_2O_7^{2-} + 3H_2S + 26H^+ \rightarrow 8Cr^{3+} + 3SO_4^{2-} + 16H_2O \tag{12}$$

The mechanisms of removal of Cr(VI) by siderite and pyrite in coal gangue may be analogous to that of chromium reduction [23]. One mechanism is that H^+ ions adsorb onto



Element	C	O	Na	Mg	Al	Si	K	Fe	Zr
mass%	6.46	50.64	2.06	3.49	10.14	17.87	0.46	6.95	2.02

Element	C	O	Al	Si	Zr
mass%	4.76	55.94	7.92	30.28	1.09

Fig. 7. SEM and EDS of coal gangue.

the surface of coal gangue particles where are electronegative contributed to free OH groups (demonstrated by the peaks at 3696 cm^{-1} and 3622 cm^{-1} in FT-IR patterns). Then, H^+ ions diffuse and make contact with siderite and pyrite embedded in the coal gangue [39]. Siderite and pyrite are decomposed and ferrous ion and, hydrogen sulphide are released into the aqueous phase where Cr(VI) is reduced to Cr(III). In this mechanism, groups of OH play a key role, which accelerates the transfer of H^+. Another mechanism may also be important to reduce Cr(VI). It includes two steps. First, anions of $Cr_2O_7^{2-}$ (Cr(VI) exists in the form of $Cr_2O_7^{2-}$ in strongly acidic solutions) bind with the positive charge supplied by H^+ (it can be identified from which the reduction of Cr(VI) become easier in solution of low pH, as 3.1.1 described) on the coal gangue surface. Second, Cr(VI) is reduced to Cr(III) by accepting electrons from adjacent electron-donors such as Fe^{2+}, H_2S and S. The two mechanisms could explain the process of Cr(VI) removal by coal gangue. In particular, reduction of Cr(VI) with sulphur can be explained by the latter mechanism which is suited to a solid/liquid phase reaction.

4. Conclusions

Coal gangue rich in siderite and pyrite can be applied to remove Cr(VI) from wastewater by reducing Cr(VI) to Cr(III) followed by chemical precipitation using ammonia and a flocculating agent. Compared with other adsorbents and reductants, the advantages of coal gangue are obvious. Coal gangue of higher reduction ability could be used to deal with a large amount of Cr(VI) sewage. Furthermore, recycling of waste is more significant than using a low-cost reagent. Removal of Cr(VI) involved three steps: release of reductant, reduction of Cr(VI), and precipitation of Cr(III). The key step in the reduction of Cr(VI) can be explained by two mechanisms. One is fit for a homogeneous reaction, for instance, the reaction of Cr(VI) with ferrous ion and hydrogen sulphide released from coal gangue in aqueous solution. The second applies to heterogeneous reactions, such as the reduction of Cr(VI) adsorbed on coal gangue with sulphur. The removal efficiency was strongly influenced by the acidity of the solution because Cr(VI) was a strong oxidant in acidic solutions and only in low-pH solutions siderite and pyrite can decompose and release ferrous ion, sulphur and hydrogen sulphide. The process of reduction of Cr(VI) fitted zero-order kinetics. The treatment capacity from both experiments and the kinetic model was more than 18.5 mg/g. Although the reduction of Cr(VI) was not impacted by the stirring rate, stirring could accelerate the reaction rate. After treatment by reduction and precipitation, the concentrations of Cr, Cr(VI) and other harmful elements released from coal gangue were all lower than the emission standards.

Acknowledgments

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