Heavy metal removal from aqueous solution using carbonaceous K$_2$S-impregnated adsorbent

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Abstract

A novel carbonaceous adsorbent for heavy metal removal was prepared from raw coal by one-step simple sulfur impregnation using K$_2$S. Raw coal was mixed with K$_2$S powder and then heated at 800°C for 30 min in nitrogen to produce K$_2$S char. The sulfur content and form in K$_2$S char were determined, and the ability of K$_2$S char to adsorb Zn^{2+}, Cd^{2+} and Pb^{2+} was examined. The K$_2$S impregnation was effective at impregnating sulfur into coal, especially in the form of elemental, thiophenic and sulfatic sulfur. The sulfur content of K$_2$S char was higher than those of raw coal and pyrolysis char. The Zn^{2+} removal in 2.4 mmol/L of Zn^{2+} solution by K$_2$S char was higher than raw coal with the removal rate of 100%. K$_2$S char adsorbed Pb^{2+} and Cd^{2+} in 24 mmol/L of Pb^{2+} and Cd^{2+} solution with the removal rate of 97% and 35%, respectively. The elution extents of adsorbed Pb^{2+} and Cd^{2+} were zero in distilled water and 27% in 0.1 mol/L HCl solution. These results indicated that an effective adsorbent for heavy metal ions was prepared from coal using K$_2$S sulfur impregnation, and that the adsorbed metals were strongly retained in K$_2$S char.

Key words: sulfur impregnation; carbonaceous adsorbent; K$_2$S; heavy metal adsorption

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Introduction

Rapid industrialization and the increase in world population have contributed to heavy metal pollution in ecosystems. Heavy metal ions (e.g., Zn^{2+}, Pb^{2+}, Cd^{2+}) have become ecotoxicological hazards of prime interest and increasing significance because of their accumulation in living organisms and high toxicities. Most industries therefore treat polluted water on-site, and ion exchange, reverse osmosis and coagulative precipitation are generally used to remove toxic heavy metal ions from wastewater (Freeman, 1989; Cheremisinoff, 1994).

Among the techniques coagulative precipitation is considered the most applicable and economical, but it produces a large amount of precipitate sludge that requires further treatment. Ion exchange and reverse osmosis can effectively reduce metal ions in wastewater, but are limited by the high cost of materials and operation. There is therefore a growing need for alternative methods for the elimination of heavy metals, such as adsorption. Recent years, various types of adsorbent have been prepared to remove heavy metals from aqueous solution.

Activated carbon widely used in waste treatments for drinking water, control of atmospheric pollution, separation of poisonous gases, and solvent recovery (Smisek and Cerny, 1970; Jankowska *et al.*, 1991). Any inexpensive carbonaceous material with high carbon content can be used as raw material for the production of activated carbons. The current trend is towards an increasing use of coal (Bansal *et al.*, 1998; Pis *et al.*, 1996). Coals are effective, economically viable precursors for the manufacture of activated carbons because they can develop a highly porous structure during the carbonization and activation processes.

Activated carbon effectively removes organic chemicals from wastewater, but is not effective in removing metals and inorganic pollutants from aqueous solution (Adhoum and Monser, 2002). It is mainly due to the relatively non-polar character of activated carbon, which inhibits the attraction between charged metal species and the surface of activated carbon (even though some functional groups may be present on the surface). Adsorption capacities and feasible removal rates must be substantially boosted by modification of activated carbon with suitable chemicals because the adsorption capacity and rate are influenced by the chemical nature of activated carbon surface (Cheremisinoff and Ellerbusch, 1980). In order to improve adsorption of heavy metals sulfur has been introduced into the material. Sulfur is a soft base that should interact with heavy metals such as Zn^{2+}, Pb^{2+} and Cd^{2+} (soft acids) rather than with oxygen (hard base) according to the Pearson theory (Pearson, 1963, 1987). Many researchers have reported the preparation of sulfurized activated carbon from commercial activated carbon or porous carbon by rapid pyrolysis or chemical pyrolysis, using pyrolysis

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in H_2S or SO_2, for the removal of heavy metals such as zinc, lead, cadmium, copper and mercury from aqueous solution (Valenzuela-Calahorro *et al*., 1990; Macias-Garcia *et al*., 1993, 1995; Gomez-Serrano *et al*., 1998; Krishnan and Anirudhan, 2002; Sugawara *et al*., 2007; Wajima *et al*., 2009). However, in these studies sulfur-impregnated adsorbent was prepared from commercial activated carbon or porous carbonacious material. When raw material is coal or agricultural waste, two-step process comprised of preparation of porous carbonaceous material and sulfur-impregnation was needed.

In this study, we attempted to prepare carbonaceous sulfur-impregnated adsorbent from coal by a one-step process involving sulfur impregnation using K_2S powder. The sulfur impregnation process to obtain char with high sulfur content was investigated and changes in the form of the sulfur during the process were determined. In addition, the ability of the obtained sulfur-impregnated char for heavy metal removal was evaluated.

1 Materials and methods

1.1 Raw material

The coal sample used in this study was Illinois No. 6 coal (Argonne Premium Coal Sample Bank). Raw coal was dried, crushed and sieved to produce particle size range 212–355 μm. Table 1 shows the proximate and ultimate analyses of raw coal.

Table 1 Chemical analyses of raw coal

Ultimate (wt.%, dry ash free basis)			Proximate (wt.%, dry basis)	
C	S	N	Volatile matter	Ash
76.7	2.7	1.5	40.3	9.8

1.2 Sulfur impregnation

The experimental procedure is shown in Fig. 1. Raw coal with or without K_2S powder was pyrolyzed to produce K_2S char or pyrolysis char.

Experimental apparatus used in this study is shown in Fig. 2. The mixture of raw coal (1 g) and K_2S powder
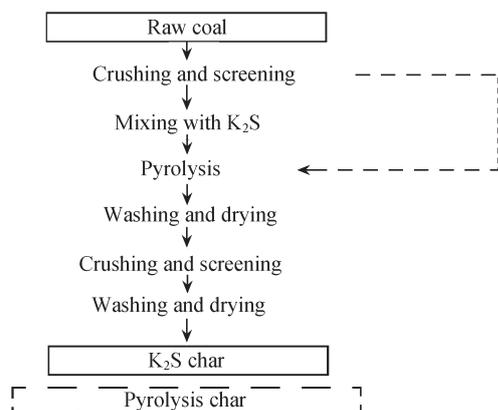
Fig. 1 Preparation of sulfur-impregnated char from raw coal.
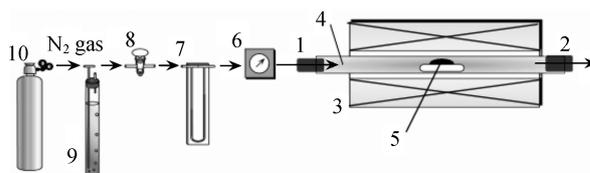
Fig. 2 Schematic diagram of reactor for pyrolysis. (1) gas inlet; (2) gas outlet; (3) furnace; (4) reactor; (5) sample; (6) wet gas meter; (7) flow meter; (8) floe valve; (9) constant head; (10) N_2 gas cylinder.

(3.6 g) or raw coal was put into a horizontal reactor (fused silica tube, 37 mm × 1 m, i.d. × length). The temperature of reactor was controlled by an electric furnace. The reactor with an N_2 atmosphere (1 L-NTP/min) was set in an electric furnace at 800°C for 30 min to pyrolyze the sample. After pyrolysis, the product was cooled to room temperature in an atmosphere of N_2. The product was then crushed and sieved to particle size range 212–355 μm. Particles were washed repeatedly with distilled water, and dried at 110°C for 12 h to prepare K_2S char.

1.3 Characterization

Sulfur contents of raw coal, pyrolysis char and K_2S char were analyzed by CHNS/O elemental analysis (2400II CHNS/O elemental analyzer, Perkin Elmer, Japan). Sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy was utilized to initially characterize and quantify the sulfur forms present before and after the pyrolysis or sulfur-impregnation. Measurements were performed at beam line X-19A at the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory, USA. Experimental procedures were described elsewhere (Huffman *et al*., 1989). Spectra were taken in fluorescent mode using a Si (111) double-crystal monochromator and a Stern-Heald-type detector (Lytle *et al*., 1985). Areas under peaks in sulfur XANES spectra were determined by a least-squares fitting procedure (EDGFIT). Areas were converted to weight percentage (wt.%) of sulfur in the different forms by a previously described calibration procedure (Taghiei *et al*., 1992; Huggins *et al*., 1992). Fourier transform infrared (FT-IR) spectra of raw coal and K_2S char were recorded on a 2000 Perkin Elmer spectrometer at wave numbers 1800–1200 cm^{-1}. Disks were prepared by thoroughly mixing 0.5 mg of sample with 100 mg of KBr in an agate mortar, and pressing the resulting mixture at 5 tons/cm^2 for 5 min. Spectra were recorded with 16 scans at a resolution of 8 cm^{-1}.

1.4 Adsorption of heavy metals

Adsorption behaviors of heavy metals by raw coal and sulfur-impregnated char were investigated. Solutions of $ZnCl_2$, $PbCl_2$ and $CdCl_2$ were used. One gram of sample was added to 100 mL of heavy metal solution, and agitated at 120 oscillations per min in a water bath at 25°C. One milliliter of slurry was removed at different time intervals for the determination of heavy metal concentration. The heavy metal ions were analyzed by atomic absorption spectrometry (AAS) (AA-6800, Shimadzu, Japan). The corresponding adsorption amounts (q_M, mmol/g) from the

material balance was calculated using the following Eq. (1):

$$q_M = \frac{(C_{M0} - C_{Mt}) \times V}{w} \tag{1}$$

where, C_{M_0} (mmol/L) and C_{Mt} (mmol/L) are the concentrations of metal ions in the solution at initial and test time, respectively; M is metal ion (Zn^{2+}, Pb^{2+}, or Cd^{2+}); V (L) is the volume of aqueous solution, and w (g) is the weight of sample added to the solution.

1.5 Desorption of heavy metals

Desorption tests were carried out on the K_2S char after it had been used in the adsorption experiments for 48 h. Briefly, saturated K_2S char that had been used in the adsorption test was added into 100 mL of distilled water or 0.1 mol/L HCl solution (Nacalai Tesque, Japan). After stirring for 24 h, the solutions were filtered. Concentrations of heavy metals in the filtrate were analyzed by AAS. The desorption extent (R_M, wt.%) was determined from the material balance using the following Eq. (2):

$$R_M = \frac{C_M \times V}{q_M \times w} \times 100\% \tag{2}$$

where, C_M (mmol/L) is the concentration of metal ions in the solution after stirring, M is metal ion (Pb^{2+} or Cd^{2+}).

2 Results and discussion

2.1 Sulfur impregnation

Figure 3a shows sulfur K-edge XANES spectra obtained from raw coal, pyrolysis char and K_2S char. Figure 3b shows least-squares fits for the spectrum of pyrolysis char as typical least-square fits. In the chars, a peak at a positive energy, corresponding to elemental sulfur, appeared. The spectrum of pyrolysis char was different to that of K_2S char.

The total sulfur content and sulfur forms were obtained using a CHNS/O elemental analyzer and least-squares analysis of sulfur K-edge XANES spectra, respectively. As shown in Table 2, the total sulfur content of raw coal (3.36 wt.%) was higher than that in pyrolysis char (2.35 wt.%), which may due to the volatilization of sulfur during pyrolysis. Differing from raw coal, pyrolysis char mainly contained elemental sulfur, thiophenic sulfur, and sulfatic sulfur. This was due to the transformation of other sulfur forms to elemental sulfur during pyrolysis. For K_2S char, the total sulfur content (8.81 wt.%) was significantly higher than that of both raw coal and pyrolysis char, and contents of all sulfur forms were increased except sulfidic sulfur. The decrease in sulfidic sulfur indicated the occurrence of the reaction which may decrease sulfidic
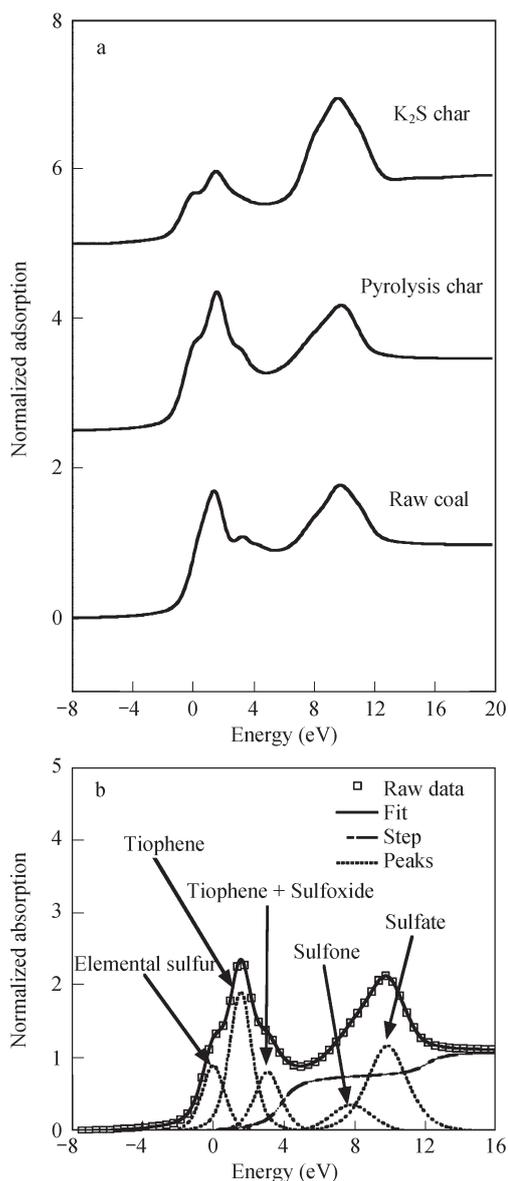

Fig. 3 Sulfur K-edge XANES spectra of raw coal, pyrolysis char and K_2S char (a), and least-squares fits for spectrum of pyrolysis char (b).

sulfur content by pyrolysis at 800°C regardless the addition of K_2S. Moreover, the content of sulfatic sulfur was half that of the total sulfur, indicating K_2S impregnation was effective in impregnating sulfur into coal, especially in elemental, thiophenic and sulfatic forms.

Figure 4 shows the FT-IR spectra of raw coal and K_2S char. The bands originating from the bonds between carbon and oxygen (e.g., C=C, COO$^-$) at about 1450 and 1600 cm^{-1} appear in the spectrum of raw coal, which was also reported by Kozłowski *et al.* (2003). These bands have decreased and a band originating from the bonds between carbon and sulfur (e.g., HSO$_3$–, CSS–) at about 1250 cm^{-1}

Table 2 Percentages of sulfur forms in raw coal, pyrolysis char, and K_2S char (wt.%)

Sulfur	Elemental	Sulfidic	Thiophenic	Sulfoxidic	Sulfonic	Sulfatic	Total
Raw coal	0.00	0.81	1.58	0.15	0.02	0.79	3.36
Pyrolysis char	0.65	0.07	1.08	0.00	0.09	0.45	2.35
K_2S char	1.77	0.00	2.15	0.38	0.44	4.06	8.81

Fig. 4 FT-IR spectra of raw coal and K$_2$S char.

Fig. 6 Adsorption of Pb^{2+} and Cd^{2+} by K$_2$S char in 24 mmol/L PbCl$_2$ and CdCl$_2$ solutions.
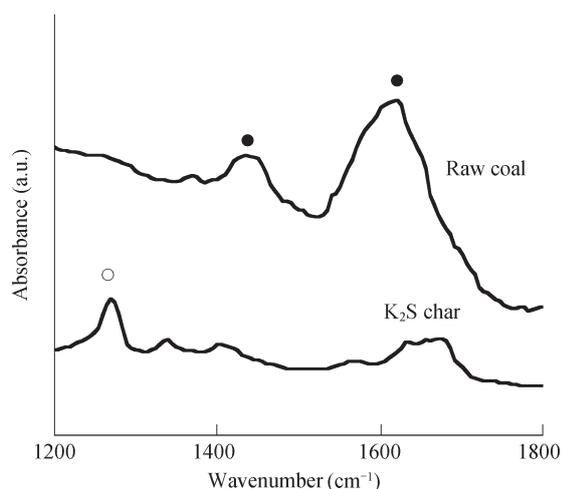
has appeared, in the spectrum of K$_2$S char. The chemical properties of K$_2$S char surface, which are important for adsorption, were completely different from those of the raw coal.

Figure 5 shows the adsorption behavior of Zn^{2+} using raw coal and K$_2$S char in 2.4 mmol/L ZnCl$_2$ solution. The adsorption amount of K$_2$S char was higher than that of raw coal, and the Zn^{2+} removal reached 100% by K$_2$S char after 24 h. We hypothesize that the carbon and oxygen functional groups on the surface of raw coal were converted to carbon and sulfur (elemental, thiophenic and sulfatic sulfur) during K$_2$S sulfur impregnation, leading to increase Zn^{2+} adsorption. These results showed that the K$_2$S method is an effective way to prepare sulfur-impregnated char with the ability to remove heavy metals.

2.2 Adsorption and desorption of heavy metals

Figure 6 shows the adsorption behaviors of Pb^{2+} and Cd^{2+} using K$_2$S char in 24 mmol/L PbCl$_2$ and CdCl$_2$ solutions. The adsorption amount of Pb^{2+} was higher than that of Cd^{2+} over the reaction time. Adsorption amounts of
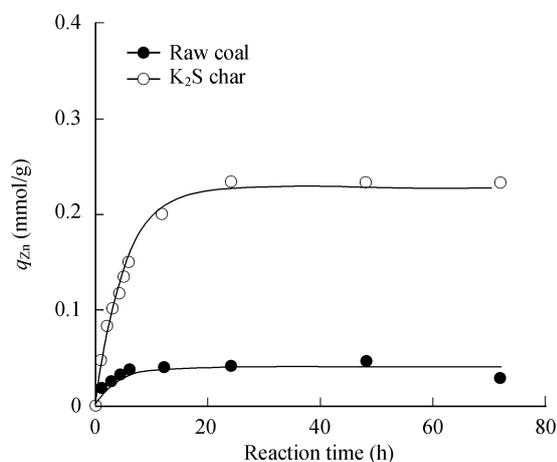
Pb^{2+} and Cd^{2+} were 2.1 and 0.7 mmol/g, respectively, at 48 h, and corresponding removal ratios were 97% and 35%, respectively. According to the Pearson theory (Pearson, 1963, 1987), Lewis acids are classified into three groups: hard, soft, and borderline. Pb^{2+} is a borderline Lewis acid, and Cd^{2+} is a soft Lewis acid. We hypothesize that the borderline group (Pb^{2+}) favors the reaction with sulfur functional groups on the surface of K$_2$S char more than the soft group (Cd^{2+}).

In desorption, elution extents of adsorbed Pb^{2+} and Cd^{2+} were zero in distilled water, and 27% in 0.1 mol/L HCl solution, indicating that heavy metals were strongly adsorbed in the K$_2$S char. This means that the adsorbent, after being used to remove heavy metals, could be discarded without elution of the adsorbed heavy metals. In refineries, coal is converted into coke to refine various metals from ores, and the metals released from coal are recovered during the conversion process. We hypothesize that carbonaceous adsorbent, after being used to remove heavy metals, could be converted to coke by mixing coal in the process and the adsorbed heavy metals could be recovered.

3 Conclusions

Sulfur-impregnated char was prepared in a one-step process using K$_2$S, and used to remove heavy metals from aqueous solution. The obtained sulfur-impregnated char contains various forms of sulfur including of elemental, thiophenic and sulfatic sulfur. Using K$_2$S char as adsorbent, the removal rate of Zn^{2+} in 2.4 mmol/L of Zn^{2+} solution was 100%, while Pb^{2+} and Cd^{2+} removal rates in 24 mmol/L of Pb^{2+} and Cd^{2+} solution were 97% and 35%, respectively. The elution extents of adsorbed Pb^{2+} and Cd^{2+} were zero in distilled water and 27% in 0.1 mol/L HCl solution. These results indicated that an effective adsorbent for heavy metal ions can be prepared from coal using K$_2$S sulfur impregnation, and that the adsorbed metals are strongly retained in the K$_2$S char.

Fig. 5 Adsorption amounts of Zn^{2+} using raw coal and K$_2$S char in 2.4 mmol/L ZnCl$_2$ solution.

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