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Removal of Mn(II) and Zn(II) ions from flue gas desulfurization wastewater with water-soluble chitosan

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ABSTRACT

Heavy metals are the most important pollutants in wastewater from dual-alkali flue gas desulfurization (FGD) system. Mn(II) and Zn(II) could predominate in the catalyzed oxidation of sulfite. So the feasibility of precipitation of heavy metal ion (Mn(II) and Zn(II)) by water-soluble chitosan was studied in a lab scale experiment. The association between chitosan and metal ions was verified through FT-IR. The pH investigation revealed that at the pH ranged from 5 to 9, there were three stages for different actions: chelation of chitosan for metal ion, precipitation of metal hydroxide and coprecipitation of metal hydroxide and chitosan–metal complex. The selective chelation of chitosan for Mn(II) and Zn(II) mixture solution was also studied. The results showed that the chelation of chitosan for Mn(II) was prior to Zn(II) in multiple component solution. Compared with the settling of metal hydroxide, the chitosan–metal complex had better separating performance. Application of chitosan solution for chelation could remove Mn(II) and Zn(II) efficiently and make it easily to separate sediment from dual-alkali FGD wastewater. On the other hand co-precipitation of the complicate heavy metal in the FGD wastewater enhanced the heavy metal removal of chitosan chelation.

1. Introduction

Dual-alkali flue gas desulphurization (FGD) process was widely used in industry to reduce the effects of scaling and plugging of the lime/limestone–gypsum FGD process [1,2]. The process commonly employed initially a sodium carbonate solution to scrub SO_2 from the flue gas and then a lime slurry to regenerate the spent scrubbing solution, which was re-circulated to remove SO_2 from the flue gas stream [3]. During the recirculation, the accumulation of chlorine and heavy metals which come from coal-fired fume results in unexpected effects, such as lowering pH of the absorption solution and making equipment corrosion and erosion [4]. The heavy metals in existence will oxidize catalytically sulfite to sulfate and result in the decrease of desulphurization efficiency [5]. Some water has to be separated regularly from dual-alkali FGD system, which is named dual-alkali FGD wastewater. The wastewater is always low pH, high concentrations of suspended solids (SS) and abundant in heavy metals (such as Mn(II), Zn(II), Ni(II), Cd(II)). Because of the serious toxicity of heavy metals toward environment, removal of heavy metals is regarded as the dominant work in FGD wastewater treatment.

Conventional methods employed to remove heavy metals contained in water streams include chemical precipitation, filtration, electrodialysis, ion exchange and ultrafiltration assisted by complexation (UFAC) [6–8]. However, electrodialysis and ion exchange plants have high maintenance and operation costs. Chemical precipitation is capable of removing trace levels of heavy metal ions but its precipitates are difficult to be separated due to their settling characteristics. UFAC, a promising process for the removal of heavy metal ions from aqueous solutions involves bonding the metals to a bonding agent (such as macromolecular species), and then separating the loaded agents from wastewater by separation processes such as membrane filtration [8]. But membrane filtration is not suitable for the wastewater with high concentrations of SS.

In recent years, chitosan has been commonly used as chelate sorbents in heavy metals removal from water and wastewater and as flocculants in solid–liquid separation [9,10]. It was clear that chitosan was a good agent for chelating numerous trace metals from wastewater [11,12]. In most of cases, chitosan was mostly used to chelate metal ions in a variety of solid forms, such as beads, flakes and membranes [11–14]. The reason was that the interaction of metal ions with chitosan dissolved in the solution did not lead to the formation of settleable flocs and metal ions remained bound onto the polymer but soluble in the solution [15]. It was necessary to get rid of the metal complex by a suitable filtration, like UFAC. The

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Nomenclature

k	equilibrium constant for the metal specie
m	mass of dried solids (g)
$q_{(pH)}$	amount of Mn(II) chelated per chitosan (mmol g^{-1})
A	density of unoccupied binding sites in the surface of chitosan, dimensionless
B	weighted average settling velocity of flocculation based on their mass fractions (m s^{-1})
C_{be}	background concentration of chelation equilibrium (mmol L^{-1})
C_{ce}	chelation equilibrium concentration (mmol L^{-1})
$C_{i,l}$	liquid phase concentration of metal specie (mmol L^{-1})
$C_{i,s}$	solid phase concentration of metal specie (mmol g^{-1})
K	contribution ratio of Mn(II) chelated by chitosan to total removal Mn(II), dimensionless
M	mass of chitosan (mg)
$S_{i,j}$	the selectivity of chitosan for ith metal species over jth metal species
V	volume of liquid (mL)

possibility of using water-soluble chitosans in decontamination of liquid radioactive wastes (LRW) of various origins from Co, Mn and Sr has been studied [16]. The result showed that chitosan in solution not only made solids flocculating but also enhanced sorption capacity of chitosan. Previously, our studies have verified that chitosan could remove Mn(II) and SS simultaneously from dual-alkali FGD regenerating process [17].

In this study, we attempted to consider the possibility of using a flocculation procedure with water-soluble chitosans for precipitation of heavy metal ions from Dual-alkali FGD wastewater. Since Mn(II) and Zn(II) were the rich metal ions (shown in Table 1) and could predominate in the catalyzed oxidation of sulfite [4,18,19], it focused on the equilibrium of chitosan solution for Mn(II) an Zn(II). Otherwise the settling characteristic of precipitate forming with the chitosan adsorption was also considered.

2. Experimental method

2.1. Materials

Chitosan was the product of deaceto-group chitin, with 85% N-acetylation degree and average molecular weight 1.0×10^5. Chitosan powder was accurately weighed 5.0 g and mixed with 500 mL of 1% acetic acids solution and kept agitating to accelerate the dissolution for about 2 h.

Two kinds of the wastewater were prepared for the experiment. The single heavy metal solutions were prepared for this experiment and contained 1 mmol L^{-1} $MnSO_4$ or 0.78 mmol L^{-1} $Zn(NO_3)_2$. The multiple heavy metal solution contained with 1 mmol L^{-1} $MnSO_4$ and 0.78 mmol L^{-1} $Zn(NO_3)_2$. The Industrial FDG wastewater used in the experiment was taken from the coal-fired plant, in which the dual-alkali wet process was engaged. The features of FGD wastewater are shown in Table 1.

Table 1
Heavy metal ions in dual-alkali FGD wastewater.

Metal	Concentration (mmol/L)	Metal	Concentration (mmol L^{-1})
Fe(II)	8.92–107.1	Cr(VI)	$\le$0.0019
Mn(II)	0.45–3.63	Cu(II)	$\le$0.0015
Zn(II)	0.015–0.15	Pb(II)	$\le 4.8 \times 10^{-4}$
Cd(II)	8.9×10^{-4}–0.017	Ni(II)	0.0017–0.085

2.2. Procedure

2.2.1. Chelation of metal ions

The influence of pH and chitosan doasge on the adsorption equilibrium was studied.

(1) Chelation of chitosan for metal ions

The experiments were carried out in the batch mode for the measurement of chelation capacities. The bottle with 250 ml capacity was filled with the single heavy metal solution or multiple heavy metal solution and the chitosan solution. The mixed liquor was immediately adjusted to a certain pH value with 1% Na_2CO_3 solution or 0.5% NaOH solution at the mixing condition with 300 rpm during 5 min. Some precipitate happened to occur in the solution at pH > 5.0. The bottles were shaken within 30–40 Hz for more than 4 h at 20 °C in a reciprocating shaker. During the reciprocating time, the dilute NaOH solution could be slowly added into the bottle to keep the change of pH less than 0.2. The solid–liquid separation was carried out by filter papers. The solution was analyzed by Atomic Absorption Spectrophotometer (AA-6300, Shimadzu, Japan), equipped with a flame atomizer (air/C_2H_2) and hollow cathode lamps of Mn/Zn. The chelation equilibrium concentration was defined as C_{ce} in mmol L^{-1}.

(2) Solubility of metal hydroxide

Due to metal hydroxide precipitation at high pH, other experiments were carried out without chitosan. The equilibrium concentration was the background concentration of chelation equilibrium and was defined as $C_{be(pH)}$ in mmol L^{-1}.

(3) Characterization

Fourier transform infrared (FT-IR) spectrometry (Nicolet Nexus 670) with an effective frequency range of 400–4000 cm^{-1} was used to analyze chitosan and chitosan–manganese complex in KBr. Chitosan used for FT-IR was dissolved into water, adjusted to a certain pH value and then dried by infrared lamp.

2.2.2. Settling characteristic of precipitate

The experiments were carried out in the batch mode for the measurement of settling rate. The precipitate from chelation of chitosan for single metal ion or the metal hydroxide precipitate was well stirred and meanwhile was transferred into a 100-mL measuring cylinder with the height of 100 mm. The height of the precipitate and water interface as a function of time was recorded to calculate the settling rate of the precipitate.

3. Results and discussion

3.1. Characterization

FT-IR was an effective tool in characterizing chitosan and its metal complex. Fig. 1 showed the FT-IR spectra of chitosan and chitosan–metal ion complex. The spectra exhibited many alterations after Mn(II) ion chelation and Zn(II) ion chelation. The major differences were: (1) the absorb band at 1640 cm^{-1} attributed to C=O group bending shifted to lower wave number (1571 cm^{-1} and 1568 cm^{-1} for Mn(II) and Zn(II) chelation, respectively) significantly after heavy metal ion chelation. (2) The absorption peaks of –OH group stretching at 1080 cm^{-1} had been lower after Mn(II) ion chelation but not shifted to lower wave number. However the absorption peaks of –OH group stretching shifted significantly to