

Adsorption removal of thiocyanate from aqueous solution by calcined hydrotalcite

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Abstract: A hydrotalcite with Mg/Al molar ratio 2 was prepared by co-precipitation method and was characterized by XRD, TG/DTA, Zeta potential and BET surface area. The hydrotalcite was calcined at 500°C, with the dehydration from interlayer, the dehydroxylation from the brucite-like layer and the decomposition of carbonate successively, transformed into the mixed oxide type. The removal of thiocyanate from aqueous solution by using the original hydrotalcite and calcined hydrotalcite (HTC-500) was investigated. The results showed that the thiocyanate adsorption capacity of calcined hydrotalcite was much higher than that of the original form. Calcined hydrotalcite was particularly effective at removing thiocyanate, and that the effective range of pH for the thiocyanate removal are between 5.5-10.0. The experimental data of thiocyanate removal fit nicely with Langmuir isotherm, and the saturated adsorption uptake was 96.2 mg SCN⁻/g HTC-500. The adsorption of thiocyanate by calcined hydrotalcite follows first-order kinetics. And the intercalation to the structure recovery for calcined hydrotalcite. But the presence of additional anions could affect the adsorption behavior of thiocyanate.

Keywords: magnesium aluminum mixed oxide; hydrotalcite; adsorption; thiocyanate

Introduction

Thiocyanate (SCN⁻) is a linear electronegative polyatomic ion, and a good example of a pseudohalide (Hughes, 1975). Due to some of its rather unique properties, thiocyanate is utilized in some industrial processes, which plays an important role in production of herbicide and insecticide, dyeing, acrylic fiber production, manufacturing of thiourea, photofinishing and electroplating. The effluents from the gold and silver mining, as well as from the gasification of coal are other major sources of thiocyanate in the environment. Thiocyanate is harmful to plants, especially to the crops, when its concentration is above 5 mg/L (Sun *et al.*, 2004). Thiocyanate can be chloridized in wastewater producing CN-Cl, which has environmental toxicity to human (Cui and Zhao, 2004). Since thiocyanate is potentially toxic to humans and aquatic organisms due to its nonhydrolyzation and nonvolatility (Evangelho and Goncalves, 2001), it must be neutralised or removed from the wastewater, prior to their release into the environment (Mosher and Figueroa, 1996). Several methods, such as adsorption, solvent extraction, oxidizing and biodegradation, have been developed for thiocyanate removal from water (Hung and Pavlostathis, 1997; Kopya *et al.*, 1997; Kociolek-Balawejder, 1999; Stott *et al.*, 2001). But biodegra-

tion of thiocyanate requires long residence time and micro-organisms are extremely sensitive to the factors such as pH, temperature and solid content; solvent extraction and oxidizing claimed appears costly (Kopya *et al.*, 1997).

Hydrotalcite, a type of layered doubled hydroxide (LDH) with a general formula of $[Mg_{1-x}Al_x(OH)_2]^+ [CO_{3/2} \cdot mH_2O]^-$, occurs as a natural mineral and can be synthesised by reacting dilute aqueous solutions of magnesium and aluminium nitrates with sodium hydroxide and sodium carbonate (Orthman, 2003). The crystal structure of hydrotalcite consists of brucite-like positively charged layers, compensated with negatively charged interlayers containing carbonate anions and water molecules to maintain overall charge neutrality (Constantino and Pinnavaia, 1995; Rives and Ulibarri, 1999). Hydrotalcite is known as anionic clay as the interlayer anions, most commonly carbonate, can be exchanged with other anions. Hydrotalcite can be transformed into the mixed oxide type undergoing dehydroxylation and decarbonation by calcination, which increase its exchange capacity and surface area (Bellotto *et al.*, 1996). The calcined product can rehydrate and incorporate anions in order to rebuild the hydrotalcite structure. So hydrotalcite as well as its calcined products have potential use as ion exchangers/adsorbents for removal of toxic anions, such as fluoride (Prakasini, 2003), anionic dyes

(Orthman *et al.*, 2003), dichromate (Das *et al.*, 2004), phenol (Ulbarri *et al.*, 1995), selenite and selenate (You *et al.*, 2001) from contaminated waters. But to our knowledge, no studies for the adsorption removal of thiocyanate by hydrotalcite and its calcined products have been reported.

In this study, hydrotalcite was synthesized. The aim of the present test was to examine the possibility of using magnesium aluminum mixed oxide, obtained by calcining of hydrotalcite at 500°C, as an adsorbent toward the removal of thiocyanate from aqueous solution.

1 Experimental

1.1 Preparation of adsorbent

The hydrotalcite was prepared by the coprecipitation method. Adding a solution containing 1.00 mol of Mg (NO₃)₂ · 6H₂O and 0.50 mol of Al (NO₃)₃ · 9H₂O (Mg/Al molar ratio 2) in 700 ml of deionized water to a vigorously stirred solution 1000 ml containing 3.50 mol of NaOH and 0.943 mol of Na₂CO₃. The final pH was 13. Heating at 65°C for 18 h to crystallize, the resulting material was separated by vacuum filtration, washed thoroughly with deionized water till the washings were neutral, the filter cake dried at 130°C overnight. The residue was calcined in air at 500°C for 4 h (this temperature was determined by the TGA/DTGA analysis) to obtain magnesium aluminum mixed oxide (denoted hereafter as HTC-500).

All chemical reagents used are AR grade.

1.2 Characterisation of the solids

The XRD patterns of the samples were recorded by a Hitachi X-ray diffractometer (D/max rA model, Japan) with an autodivergent slit fitted with a graphite monochromator using Cu-K_α radiation at a scanning speed of 2°/min, operated at 40 kV and 20 mA.

The thermal analysis(TGA/DTGA) of the sample was carried out at a heating rate of 20°C/min up to 700°C using a Mettler Toledo Simultaneous TGA/SDTA851 in the range 25–700.

The specific surface area of the sample outgassed at 110°C in vacuum was determined by the N₂ adsorption/desorption method at liquid N₂ temperature (196°C) using a Micromeritics ASAP 2000 equipment.

The zeta potential of particles of hydrotalcite or HTC-500 in water at different pH values was measured by a micro-electrophoretic mobility detector (DXD-II model). The suspensions of hydrotalcite or HTC-500 of 2 g/L were prepared, respectively. The pH of the suspension was adjusted with NaOH or HNO₃. Then the electrophoretic mobilities of hydrotalcite or HTC-500 particles were measured in glass

electrophoresis tank, Zeta potentials were calculated based on the measured electrophoretic mobilities of the particles with the Smoluchowski equation (Chen, 1984).

1.3 Batch adsorption experiment

The thiocyanate removal experiments were carried out by a batch method. The thiocyanate solutions were prepared by dissolving KSCN in deionized water, diluting the prepared standard solution(500 mg/L) to desired concentrations. The pH of the thiocyanate solution was adjusted using HNO₃ and NaOH. A predetermined amount of the hydrotalcite or HTC-500 as adsorbent was added to 50 ml solution (with known initial thiocyanate concentration and pH value) in a 100 ml closed flask. The suspension was shaken at 100 r/min in a Jintan SHZ-82 type thermostated shaker. After the given contact time for adsorption, the solid material was separated by centrifugation (using a LG10-2.4A centrifuge). The remaining concentration of thiocyanate in solution was determined by Shimadzu UV-1601 type UV-Vis spectrophotometer at 480 nm, following the ferric nitrate method in acidic environment (modified by nitric acid; Cui and Zhao, 2004).

2 Results and discussion

2.1 Characterisation of the hydrotalcite adsorbent and the HTC-500

Fig.1 shows the XRD patterns for the hydrotalcite and the HTC-500. Fig.1a shows sharp and symmetric peaks at lower 2θ values, which are characteristic of hydrotalcite, and the material consists of one phase only. But when the material is calcined at 500°C the layered hydrotalcite structure is lost, and a phase change is observed (Fig.1b), the hydrotalcite is converted to mixed oxides of magnesium and aluminium. After thiocyanate adsorption from aqueous solutions, reconstruction of the layered structure (Fig.1c) is observed.

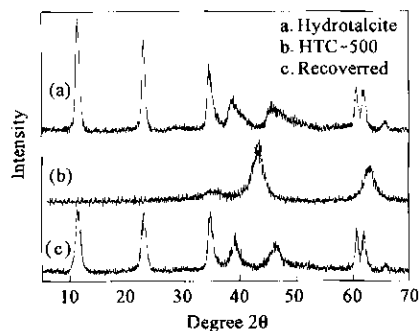


Fig.1 XRD patterns of samples

The result of the thermo analysis of hydrotalcite in present test (TG/DTA) is shown in Fig.2. There are two independent endothermic peaks in DTA curve and corresponding two mass loss step in TG curve. The endothermic peak at 233°C detected in DTA curve are ascribed to losses of interlayer water, The endothermic peak at 412°C are attributed to the dehydroxilation from the brucite like layer and the decomposition of most of the carbonate, with consequent evolution of water and CO₂ respectively. A very small mass loss above 500°C (ca. 2.6 mass%) can be attributed to the decomposition of residual hydroxyl groups.

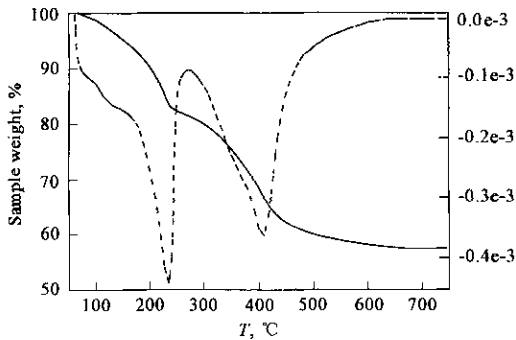


Fig.2 TG and DTA curves of hydrotalcite
— sample weight (%); ---- DTA

As a result, a temperature of 500°C for the calcination of the hydrotalcite is sufficient to eliminate most of the carbonate anions. Too higher temperatures may hinder the structural reconstruction (Stanimirova *et al.*, 1999), reduce the capacity of the material, so the calcine temperature was chosen as 500°C.

The surface area of hydrotalcite and HTC-500 were determined by the single point BET method and were found to be 81.2 m²/g and 306.5 m²/g, respectively.

The results of Zeta potential at various pHs for hydrotalcite and HTC-500 in suspension were presented in Fig.3. It indicated that the isoelectric

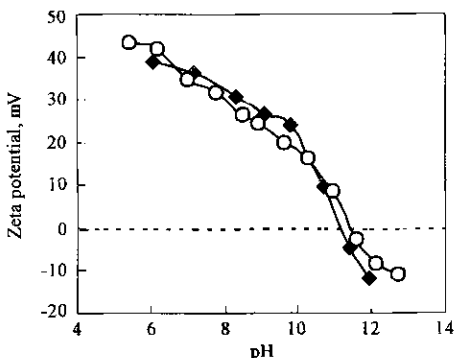


Fig.3 Relationship between Zeta potential of hydrotalcite or HTC-500 and pH in water

point(IEPs) for hydrotalcite and HTC-500 are reached at pH 11.8 and 11.6, respectively. And hydrotalcite and HTC-500 have surface residual positive charge in suspension at pH under the IEP.

2.2 Equilibrium study of thiocyanate adsorption

The adsorption isotherms of thiocyanate on original hydrotalcite and calcined hydrotalcite, hydrotalcite, at 25°C are illustrated in Fig.4. Equilibrium experiments showed that HTC-500 had a much higher adsorption capacity than that of original hydrotalcite.

The experimental data were fitted to the isotherm models of Langmuir and Freundlich respectively. The models are represented mathematically as follows:

$$q = q_m \frac{KC}{1+KC}; \quad q = kC^{\frac{1}{n}}$$

where q is the amount of adsorbed thiocyanate on adsorbent; q_m is the saturated adsorption of thiocyanate (mg/kg); K is a constant of the Langmuir isotherm and C is the concentration of thiocyanate solution; k and n are parameters of the Freundlich isotherm.

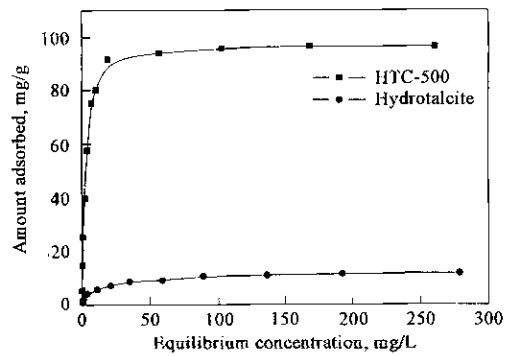


Fig.4 Equilibrium modeling for the adsorption of thiocyanate (by hydrotalcite and HTC-500)

Table 1 presents the parameters values of the Langmuir and Freundlich isotherm. As a result shown in Fig.4, these data nicely fit a Langmuir isotherm (correlation coefficients $R^2 = 0.997$ and 0.990 for HTC-500 and hydrotalcite respectively). The q_m for HTC-500 was 96.2 mg/g, near 10 times of the one for the original hydrotalcite.

The earlier reported results for the adsorption of anions on hydrotalcite indicate that the two mechanisms involved in the adsorption process are surface

Table 1 Langmuir and Freundlich isotherm parameters for adsorption of on original hydrotalcite and calcined hydrotalcite

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m , mg/kg	K	R^2	k	n	R^2
HTC-500	96.2	0.578	0.997	25.17	2.79	0.834
Hydrotalcite	10.4	0.258	0.990	1.79	2.61	0.891

adsorption and anion exchange (Chatelet *et al.*, 1996; Orthman *et al.*, 2003). In this study the surface adsorption meant thiocyanate may be adsorbed on the hydrotalcite's surface. The parameter of adsorbent surface area plays a key role in this mechanism. The anion exchange adsorption mechanism was a special property for hydrotalcite and meant thiocyanate attempt to enter the interlayer region of hydrotalcite by anion exchange with interlayer carbonates. But the affinity of hydrotalcite's brucite-like layers for polyvalent anions higher than that for monovalent anions (Miyata, 1983; Chatelet *et al.*, 1996). So it is difficult and almost impossible that the carbonates in interlayer of hydrotalcite to be exchanged by monovalent anions, thiocyanate, i.e., the adsorption of thiocyanate on the hydrotalcite attributed mainly to the surface adsorption.

But when heated at 50 °C, hydrotalcite containing carbonates as the interlayer anion is decomposed into magnesium and aluminium oxide solid solution (Fig.1b) with the lossing of interlayer water, the dehydroxilation from the brucite like layer and the decomposition of most of the carbonate, with consequent evolution of water and CO₂ respectively. The calcined product HTC-500 can rehydrate and incorporate anions, to rebuild the initial layered doubled hydroxide structure when the calcined sample was dispersed in aqueous solutions containing anions (Stanimirova *et al.*, 1999). The ydrotalcite-like compound that thiocyanates as the interlayer anion (Fig.1c) were rebuilt during the adsorption of thiocyanate on HTC-500. So, in the case of the adsorption of thiocyanate on HTC-500, it was suggested that the process may not be described as a pure adsorption, but as a conjunction of surface adsorption and intercalation.

The surface area of HTC-500 was higher than that of original hydrotalcite, and thiocyanate could enter the interlayer region of ydrotalcite-like compound by intercalation mechanism. Therefore, the adsorption capacity of HTC-500 for thiocyanate was increased by increasing surface area as well as available binding sites due to the calcining .

2.3 Effect of pH on thiocyanate adsorption

The adsorption of thiocyanate on HTC-500 was found to be a function of pH within the range of 2.5–13 (Fig.5). The removal of thiocyanate from the solution was favoured when the solution pH was between 5.5–10.

At higher pHs, due to the OH⁻ competitive adsorption with SCN⁻ on HTC-500, especially when the pH was above the IEP, the adsorbent surface

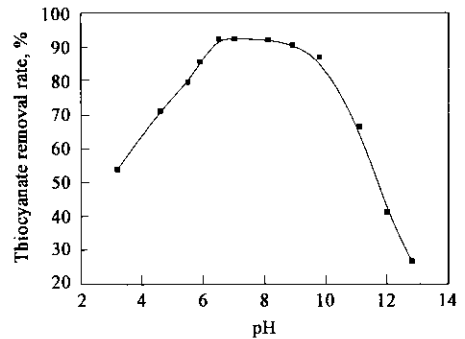


Fig.5 Effect of pH on thiocyanate removal rate

becomes negatively charged (Fig.3) and will be associated with positively charged ions of the solution. So the thiocyanate adsorption declined when the pH was above 10.0.

The decreased thiocyanate adsorption when the solution pH was less than 4.5, may be caused by the dissolution of HTC-500 at low solution pH (Allada *et al.*, 2002).

2.4 Adsorption kinetics

Adsorption rate is an important factor evaluating the application of adsorbents. The variation of thiocyanate adsorption from the aqueous medium was studied as a function of time (Fig.6). It was found that 91% of thiocyanate could be adsorbed within the initial 3 h(optimum time).

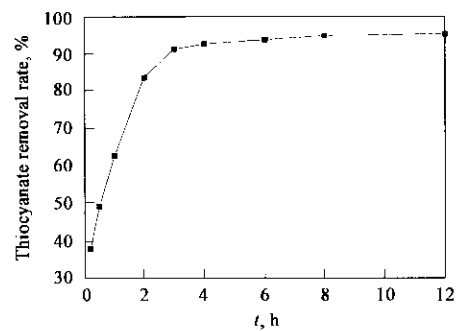


Fig.6 Plot of thiocyanate removal with the contact time

The adsorption of thiocyanate onto HTC-500 follows Lagergren's first-order rate equation, which is represented as

$$\log(X_c - X) - \log(X_c) = -K_{\text{ads}} t / 2.303$$

In which, K_{ads} is the first-order rate constant; X is the amount of thiocyanate onto adsorbent (mg SCN⁻/g dried HTC-500).

The plot of $\log(X_c - X)$ vs. t (Fig.7) proves that it follows first-order kinetics. The first-order rate constant, K_{ads} , can be correlated as $6.6 \times 10^{-1} \text{ h}^{-1}$ or $1.1 \times 10^{-2} \text{ min}^{-1}$ for initial thiocyanate concentration 50 mg/L, adsorbent dose 2 g/L, temperature 25 °C and pH 6.5.

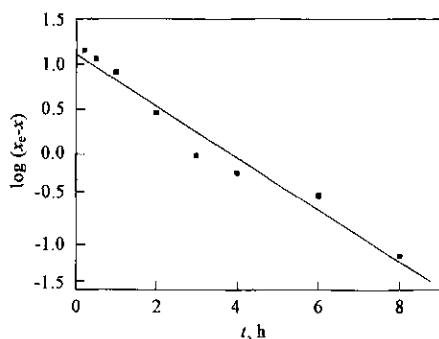


Fig.7 Plot of adsorption rate with Lagergren equation

2.5 Effect of competing anions on thiocyanate adsorption

Wastewaters contain normally many ions such as phosphate, sulfate, chloride and nitrate. They compete with thiocyanate to be adsorbed onto HTC-500. Fig.8 indicates that the presence of additional anions could affect the adsorption behavior of thiocyanate.

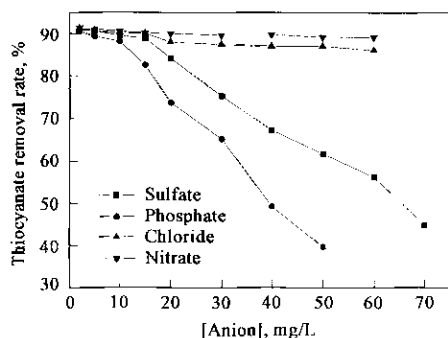


Fig.8 Effect of additional anions on thiocyanate removal

The percentage of thiocyanate adsorption remains almost constant up to a 15 mg/L of phosphate concentration, thereafter decreases, and finally reaches 44.8% when the same is increased to 70 mg/L. In the case of sulfate the adsorption(%) of thiocyanate decreases when concentration is above 10 mg/L and reaches 39.7% when sulfate concentration is 50 mg/L. But the presence of chloride and nitrate affect the adsorption of thiocyanate very little. The thiocyanate adsorption in presence of interfering ions increased in the order: phosphate > sulfate > chloride > nitrate. The effect of these anions towards adsorption may be related to the their affinity towards HTC-500. And layered double hydroxides have greater affinities for anions with higher charge density (Miyata, 1983; Chatelet *et al.*, 1996).

3 Conclusions

The magnesium aluminum mixed oxide, obtained

from the thermal decomposition of hydrotalcite at 500°C, can be used as an effective adsorbent for the removal of thiocyanate. But the presence of additional anions, especially polyvalent anions, such as phosphate and sulfate, could affect the adsorption behavior of thiocyanate. The above studies show that calcined hydrotalcite was particularly effective at removing thiocyanate, and that the effective range of pH for the thiocyanate removal are between 5.5–10.0. In the adsorption the thiocyanate removal rate exceeding 91% with equilibrium time of 3 h at pH 6.5 was obtained. The experimental data of thiocyanate removal fit nicely with Langmuir isotherm, by which the saturated adsorption uptake of 96.2 mg SCN⁻/g HTC-500. The Lagergren plot shows that the adsorption of thiocyanate by calcined hydrotalcite follows first-order kinetics.

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