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Metal oxides as dual-functional adsorbents/catalysts for Cu^{2+}/Cr(VI) adsorption and methyl orange oxidation catalysis

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ABSTRACT

The LDO, calcined product of the Mg/Al-CO_3 hydrotalcite, was used as a dual-functional adsorbent/catalyst material for the removal of binary heavy metal ions and the catalytic degradation of methyl orange (MO). The adsorption properties for Cu^{2+} cations and Cr(VI) anions were investigated in depth in single and co-adsorption systems. The results showed that the LDO demonstrated 0.80 and 2.90 mmol/g adsorption capacities in single Cu^{2+} (1.6 mmol/L) and Cr(VI) (4.0 mmol/L) systems, respectively. In co-adsorption system, $Cu_2(OH)_3Cl$ precipitation, isomorphic substitution of Mg^{2+} sites by Cu^{2+} and intercalation of $CrO_4{}^{2-}$ into the interlayers played important roles. On the LDO, Cu^{2+} and Cr(VI) presented synergetic effect, resulting in an increase in both Cu^{2+} and Cr(VI) adsorption capacities. In addition, the spent adsorbents were employed as a catalyst for methyl orange (MO) degradation. The Cr-Cu-RLDO, a calcined product of the spent adsorbent in the co-adsorption system, indicated the high activity with 86.5% degradation rate of MO in the presence of H_2O_2. The existence of Cu and Cr elements in the catalyst was one of the causes of the enhanced degradation of MO.

1. Introduction

Water pollution of heavy metals is considered to be a serious menace to the environment and especially to human health in view of their persistence, bio-magnification, non-degradation and toxicity. Industrial used water is one of the major sources of heavy metals pollution, which contains toxic metals such as Cr, Cu, As, Pb and Ni [1]. One effective way of removing heavy metals is the adsorption by various materials such as activated carbon [2], biomaterials [3,4] and clay minerals [5,6]. The process of adsorption implies that an adsorbent binds heavy metal ions by physical attractive forces, ion exchange and chemical binding. Hydrotalcite materials are anionic clays with layered mixed hydroxides containing exchangeable anions. Their abundance in nature, low cost, high anion exchange capacity, good thermal stability, large surface area and regeneration ability make them suitable for wastewater treatment. One of the properties is the high anion exchange capacity for various water contaminants, which is generally used for the removal of anions from aqueous solutions and wastewaters [7,8]. However, hydrotalcites are unfavorable for the removal of cations such as heavy metals. Recently, there are few reports on the adsorption for metal cations via interlayer chelating and surface modification using hydrotalcites as adsorbents, indicating that they could remove heavy metal cations [9,10]. However, the high cost and manipulating complexity have limited their use in the wastewater treatment.

In the practical environment, contaminated water system usually contains a mixture of heavy metals rather than pure heavy metal ions. As to some heavy metal ions (Cr and As), they exist in wastewater mainly in the form of anionic metal complexes, and most of heavy metal ions exist as cations. It is a bit difficult for most adsorbents to eliminate simultaneously both anionic metal complexes and ionic metal species from water. Only few are dedicated to the co-adsorption behavior of cations and anions in the binary heavy metal ions solutions. To adsorb binary heavy metal ions, ion exchange resins were prepared by modified biomaterials. The removal efficiency of the resins as adsorbents for the removal of both chromate ($CrO_4{}^{2-}$) anions and copper (Cu^{2+}) cations was obviously improved [11]. To the best of our knowledge, there are few reports on the removal of mixed heavy metal anions and cations by hydrotalcites. In addition, when adsorbents reach their saturation limit, they are usually taken to a landfill and discarded. It will cause the secondary pollution if the spent adsorbents are placed in open air place, for the non-biodegradability of heavy metals [12,13]. This has motivated the development of the spent adsorbent reuse to make treatment process more environmentally friendly and ensure their economic feasibility. So it appears attractive to combine adsorption with catalytic degradation in water treatment system, in which the heavy metal contaminants are removed from wastewater by adsorption, and then the

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Nomenclature

LDH	Mg/Al-CO_3^{2-} hydrotalcites with Mg/Al molar ratio of 4.0.
LDO	calcined product of LDH.
RLDH	the rehydration product of LDO.
RLDO	calcined product of RLDH.
Cr-RLDH	the spent adsorbent in the reaction solution with 4.0 mmol/L Cr(VI).
Cu-RLDH	the spent adsorbent in the reaction solution with 1.6 mmol/L Cu^{2+}.
Cr-Cu-RLDH	the spent adsorbent in the co-adsorption system of 1.6 mmol/L Cu^{2+} +4.0 mmol/L Cr(VI).
Cr-RLDO	calcined product of Cr-RLDH.
Cu-RLDO	calcined product of Cu-RLDH.
Cr-Cu-RLDO	calcined product of Cr-Cu-RLDH.

spent adsorbents are reused as catalysts to degrade organic contaminants in wastewater.

Previous studies mainly focused on how to make heavy metal pollutants controlled effectively by hydrotalcites instead the reuse of the spent adsorbents. Besides, to our best knowledge, few information is available about hydrotalcite powders used both as adsorbents for heavy metal ions and catalysts (spent adsorbents) for organic dye degradation. In this study, the calcined Mg/Al-CO_3^{2-} hydrotalcite (LDO) was used as dual-functional adsorbent/catalyst material for the removal of binary heavy metal ions and degradation of organic dye. First, the adsorption properties of the LDO as a adsorbent for Cu^{2+} and Cr(VI) in single and co-adsorption systems were studied, and the adsorption mechanisms were explained based on the characterization results. Secondly, the spent adsorbents were reused as catalysts for the degradation of Azo dye methyl orange (MO), and the catalytic activity was investigated.

2. Experimental

2.1. Materials

All the reagents/reactants were of analytical grade and solutions were prepared with deionized water. 0.1 mol/L NaOH and HCl solutions were used for pH adjustment. A pH electrode for high temperature (Mettler Toledo S40K) was used for pH measurements.

2.2. Preparation of the hydrotalcites

Mg/Al-CO_3^{2-} hydrotalcites with Mg/Al molar ratio of 4.0 (LDH) were prepared by urea hydrolysis ([urea]/[NO_3^-] molar ratio of 4.0) according to the literature previously described [14]. In our previous works, it was found that the LDH calcined at 500 °C had the largest Cr(VI) adsorption capacity [15]. So, part of the precursor LDH was calcined at 500 °C for 4 h, which was denoted as LDO (adsorbent). 100 mg LDO was suspended in 100 mL of Na_2CO_3 (0.1 mol/L) solution and kept under magnetic stirring at 50 °C for 48 h. The rehydration product was centrifugated, washed to neutral, and then dried, which were denoted as RLDH. Part of the RLDH was calcined again at 500 °C for 4 h, which was denoted as RLDO as a catalyst (control). All the calcined samples were kept in a dryer for the subsequent experiments.

2.3. Adsorption tests

2.3.1. Adsorption of single metal ions

In our preliminary works, it was found that the adsorption equilibrium times were 2 h for Cr(VI) anions and 5 h for Cu^{2+} cations in a given concentration ranges of Cr(VI) anions and Cu^{2+} cations, respectively. And according to our previous works [15] and preliminary experiments, the adsorption of Cr(VI) was carried out using the LDO as an absorbent in the $K_2Cr_2O_7$ solution. The initial Cr(VI) concentrations were 1.0∼12.0 mmol/L, and the adsorbent dose 1.0 g/L. The $K_2Cr_2O_7$ solution was pre-adjusted to pH 5.5. Under magnetic stirring, the adsorption was carried out at 50 °C for 2 h in order to attain the adsorption equilibrium. After the reaction, the reaction solution was centrifuged at 7000 rpm for 3 min, and the supernatant was measured by a pH electrode and kept for Cr(VI) measurement, and the residue was washed three times. The solutions produced from the washing steps were stored for Cr(VI) determination. The Cr(VI) determination was carried out by UV–vis spectrophotometric method (Hitachi U-2910) using 1,5-diphenylcarbazide as color indicator at 540 nm in acid medium by following APHA, AWWA standard methods. The treated residue (spent adsorbent) in the reaction solution with 4.0 mmol/L Cr(VI) was denoted as Cr-RLDH.

The $CuCl_2$ solutions with initial Cu^{2+} concentrations range from 0.4∼3.2 mmol/L were prepared, which were adjusted to pH 4.5. 1.0 g/L LDO was added into the $CuCl_2$ solution with specified Cu^{2+} concentration under magnetic stirring at 50 °C for 5 h to attain the adsorption equilibrium. After the reaction, the reaction solution was centrifuged at 7000 rpm for 3 min, and the supernatant was measured by a pH electrode and kept for Cu^{2+} measurements by the atomic absorption spectrophotometer (Hitachi, Z-8000). The residue was washed for three times and the solution produced from the washing steps was stored for Cu^{2+} determination. The treated residue in the reaction solution with 1.6 mmol/L Cu^{2+} was denoted as Cu-RLDH. All experiments were carried out in triplicate on average and the deviation of the mean was less than 5%. Parts of the Cr-RLDH and Cu-RLDH were calcined at 500 °C for 4 h, and the calcined products were denoted as Cr-RLDO and Cu-RLDO as catalysts, respectively. The Cr(VI)(or Cu^{2+}) adsorbed (η, %) and equilibrium adsorption capacity (q_e) calculated as follows, respectively.

$$\eta\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100\%; \quad q_e = \frac{V(C_o - C_e)}{m}$$

where q_e was the adsorption capacity at equilibrium time (mmol/g), V was the volume of the reaction solution (L), and m was the mass of the adsorbent (g). C_o was the initial Cr(VI) (or Cu^{2+}) concentration (mmol/L), and C_e the Cr(VI) (or Cu^{2+}) concentration at equilibrium time (mmol/L).

2.3.2. Co-adsorption of the binary ions

In order to determine the interactive effect of the LDO adsorption of Cr(VI) anions and of Cu^{2+} cations, the assay was performed by adsorbing the binary ions on the LDO for 3.5 h in order to reach the adsorption equilibrium. Two parts of adsorption experiments were carried out as follows. First part was the effect on the uptake of Cu^{2+} with Cr(VI) present in the solution, where the initial concentration of Cu^{2+} remained constant at 1.6 mmol/L and the concentration of Cr(VI) varied from 1.0 to 12.0 mmol/L (I system). Second part was the effect of Cu^{2+} on the adsorption of Cr(VI). In this section, the initial concentration of Cr(VI) was fixed at 4.0 mmol/L, whereas the concentration of Cu^{2+} was changed from 0.4 to 3.2 mmol/L (II system). The spent adsorbent in the co-adsorption system of 1.6 mmol/L Cu^{2+} +4.0 mmol/L Cr(VI) was denoted as Cr-Cu-RLDH. Part of the Cr-Cu-RLDH was calcined at 500 °C for 4 h, and denoted as Cr-Cu-RLDO as a catalyst.

2.4. Characterization of samples

Powder X-ray diffraction (XRD) pattern was obtained in the 2θ range 5∼70° using a Rigaku D/MAX-3C instrument with CuKα source (λ = 0.1541 nm). FTIR spectrum was recorded on Perkin–Elmer Spectrum One B instrument using KBr pellet technique. Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) (S-4800-I, HITACHI, Tokyo, Japan) were used to characterize the surface