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High uptake of Cu^{2+}, Zn^{2+} or Ni^{2+} on calcined MgAl hydroxides from aqueous solutions: Changing adsorbent structures

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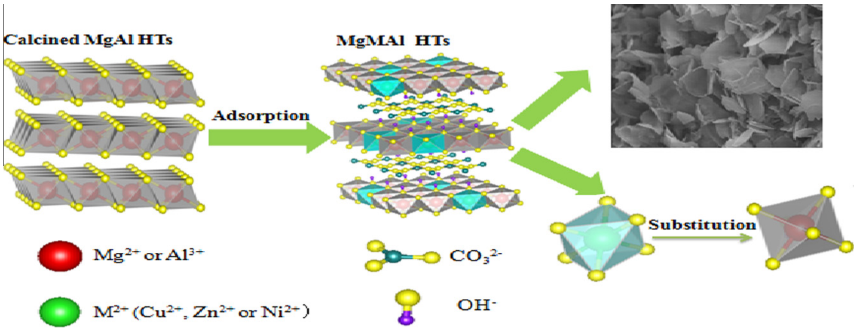
HIGHLIGHTS

- High affinity and adsorption capacity of CHTs were in order of $Zn^{2+} > Ni^{2+} > Cu^{2+}$.
- Pseudo-second-order and Langmuir models well described kinetic and isotherm data.
- The uptake process for Cu^{2+}, Zn^{2+} or Ni^{2+} was spontaneous and endothermic.
- The adsorbent could be used circularly 4 times efficiently.
- Final removal of metal ions by reassembling hydrotalcites structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Although previously a variety of studies have proposed the removal of anions and organic matters from contaminated water by calcined hydroxides (CHTs), their role in uptaking potentially toxic metal ions from effluents had rarely been investigated. In the present study, simulated wastewater containing Cu^{2+}, Zn^{2+} or Ni^{2+} was used to investigate the adsorption performance of CHTs. Langmuir and Freundlich isotherm models were employed to fit the equilibrium experiments, and it was found that the Langmuir model was more appropriate to describe the adsorption isotherm. The maximum adsorption amount was higher than some other adsorbents, specifically, being 6.583, 7.535 and 6.152 mmol/g for Cu^{2+}, Zn^{2+} or Ni^{2+} under the proposed conditions. For kinetic data, the pseudo-second-order kinetic model appeared to be the best-fitting model compared to the pseudo-first-order and Elovich models. Thermodynamic analysis revealed that Cu^{2+}, Zn^{2+} or Ni^{2+} sorption on CHTs was spontaneous and endothermic. In the reusability study, the sorption capacity of the adsorbent did not vary remarkably in the initial four sorption/calcination cycles for Cu^{2+}, Zn^{2+} or Ni^{2+} removal. By virtue of X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron dispersive X-ray analysis (EDX), it was speculated that the adsorption mechanism for Cu^{2+}, Zn^{2+} or Ni^{2+} consisted of two steps: First, potentially toxic metal ions formed into hydroxide precipitations and adhered to the surfaces of adsorbents with high alkalinity. Second, the hydroxides participated in the process of adsorbents reconstructed the hydrotalcites structures through isomorphous substitution.

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1. Introduction

Environmental problems have been a major global concern for the last few decades [1]. Increasing worldwide water contamination has become one of significant environmental problems. Specifically, potentially toxic metals, such as copper, zinc, nickel, cadmium and lead, etc., which cannot be decomposed may gradually accumulate in environment and living organisms, and consequently result in severe diseases or even death. There are wide industrial sources of these potentially toxic metals, such as metal fabrication, mining, plating, batteries, paints, and so on. Therefore, wastewater regulations should be toughed to promote the development of efficient processes. The remediation of potentially toxic metals in wastewater urgently needs to be resolved [2,3].

So far, various treatment technologies have been employed for disposing potentially toxic metals in effluents, including chemical precipitation, adsorption, filtration, reverse osmosis, evaporation, etc [4,5]. Among them, adsorption is one of the most promising techniques due to its advantages of operation simplicity, high efficiency, low cost and potential for regeneration [6]. Moreover, adsorption reactions are prone to controlling the rate and transporting of metal ions. Due to the large surface area, high porosity and specific structure, layered double hydroxides (HTs) have been extensively utilized as efficient adsorption materials for adsorbing various anions [7–9] and metal cations [10–12]. Modified HTs with chelating ligands such as humate hybrid [13], diethylenetriaminepentaacetic acid (DTPA) [14] and ethylenediaminetetraacetate (EDTA) [15] were extensively studied recently in terms of metal cations adsorptions, limited promotion on the adsorption efficiency was found compared to HTs. Since calcined HTs (CHTs) possess a number of active sites, large surface area and the character of refactoring hydrotalcites structures in aqueous solution, they demonstrate higher adsorption capacity of anions than HTs, which had been confirmed in many previous studies [16,17]. It is worth noting that little attention has been paid to the removal of metal cations by CHTs [11], although CHTs may possess higher removal efficiency for metal ions comparing with HTs. The calcinations of HTs can greatly promote the adsorptions of potentially toxic metals ions, as reported by Yuan et al. [18]. In order to provide more relevant evidences and to remove metals ions more effectively, the studies on remediating wastewater containing potentially toxic metals ions by CHTs became important.

This work committed to the adsorption of metal cations (Cu^{2+}, Zn^{2+} or Ni^{2+}) by CHTs, which are obtained by calcining HTs. The HTs is a class of two-dimensional nanostructure anionic clays. The crystals of HTs are composed of brucite-like layers ($Mg(OH)_2$), where the divalent magnesium cations locate in the center of edge-sharing octahedral with hydroxyl anions at their vertices and planar, and neutral layers were formed [17,19]. When divalent metal ions are substituted by trivalent metal ions, the lamella shows positive residual charge. According to the charge neutrality principle, anions intercalate the interlayer regions together with water molecules, which promoted stacking of the sheets. Finally, a hydrotalcites type structure was formed. CHTs, as one class of mixed metal oxides, could utilize anions and metal cations in aqueous solution to reconstruct the lamellar structures of HTs, which was called "memory effect" [20]. When utilizing CHTs in purifying wastewater with anions or potentially toxic metals ions, metal cations could be removed by incorporating new sheets with isomorphous substitution, and anions could be removed by chelating or intercalating the interlayer regions with electrostatic attractions. The general formula of HTs and CHTs can be expressed as $[M_{1-x}{}^{2+}\ M_x{}^{3+}\ (OH)_2]\ (A^{n-})\ {}_{x/n}{\cdot}yH_2O$ and $(M_{1-x}{}^{2+}\ M_x{}^{3+}\ O_{1+x/2})$, respectively, where, M^{2+} and M^{3+} are divalent and trivalent cations, A^{n-} is the n-valent anion, and x is equal to the value of $M^{3+}/(M^{2+}+M^{3+})$ [21]. The uptake process of divalent cations (N^{2+}) on CHTs can be expressed by Eq. (1) [22,23]:

$$\begin{aligned} &M^{2}_{1-x} + M^{3+}_{x}O_{1+x/2} + (x/n + 2y/n)A^{n-} + (m + 1 + x/2)H_2O \\ &\quad + yN^{2} \rightarrow M^{2+}_{1-x}N^{2+}_{y}M^{3+}_{x}(OH)_2A_{(x+2y)/n} \cdot mH_2O + xOH^{-} \end{aligned} \tag{1}$$

The objective of this study was to evaluate the adsorption capacity of Cu^{2+}, Zn^{2+} or Ni^{2+} on MgAl CHTs in single metal cation aqueous system. Adsorption equilibrium, kinetics and thermodynamics were analyzed to understand the adsorption mechanism and adsorption capacity for potentially toxic metals ions. The regeneration performance, one of the crucial characteristics for adsorbents in practical remediation applications, was also investigated. Moreover, the adsorption mechanisms for metal ion were further explored and described in detail.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical pure. All water was deionized. The synthesized nitrate solutions of copper, zinc and nickel, with the concentration of 10,000 mg/L, were used to stock solutions. The HNO_3 or NaOH solution (0.1 mol/L) was prepared to adjust the pH of solutions.

2.2. Synthesis of MgAl HTs and MgAl CHTs

The $Mg_3Al–CO_3$ HTs were prepared by co-precipitation method [24]. In this method, the 400 mL solution containing $Mg(NO_3){\cdot}6H_2O$ (0.12 mol) and $Al(NO_3)_3{\cdot}9H_2O$ (0.04 mol) was added drop wise to 400 mL of deionized water at room temperature. Simultaneously, the another mixture solution containing 1.6 mol of NaOH and 0.1 mol of Na_2CO_3 in 250 mL of water was added with vigorously stirring [19]. The pH of the reaction mixture was maintained at 10 ± 0.5. After stirring 2 h, the resulting slurries were separated by vacuum filtration, and then were aged at 80 °C for 24 h. The content of hydrotalcites was obtained by drying the above products. The calcined production (CHTs) was prepared by heating hydrotalcites (HTs) in a muffle furnace at 450 °C for 2 h.

2.3. Adsorption kinetics

Kinetics experiments were carried out at specific reaction time intervals of 0, 10, 30, 50, 90, 120, 180, 240 and 300 min in a thermostat shaker under constant shaking (150 rpm) at 25, 35 and 50 °C. The initial concentration of Cu^{2+}, Zn^{2+} or $Ni^{2+}$was 200 mg/L, the volume of solution was 100 mL and the sorbent dosage was 0.5 g/L. Initial pH value of the solution was adjusted by 0.1 mol/L HNO_3 or NaOH solution. Under a certain reaction time and temperature, 2 mL of reaction solution was taken and filtered by 0.22 μm membrane. The residual metal ion concentration in the filtrate was analyzed by flame atomic absorption spectrophotometer.

The uptake quantity of Cu^{2+}, Zn^{2+} or Ni^{2+} on CHTs at time t was determined by the following equation [25]:

$$q_t = (C_o - C_t)V/m \tag{2}$$

where q_t is the quantity of Cu^{2+}, Zn^{2+} or Ni^{2+} adsorbed on CHTs at the time t (mg/g), $q_e = q_t$ when adsorption reaches equilibrium, V is the volume of solution (L), C_o and C_e are the initial and the time t concentration of Cu^{2+}, Zn^{2+} or Ni^{2+} (mg/L), respectively, m is the mass of adsorbent (g).