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Express Al/Fe oxide–oxyhydroxide sorbent systems for Cr(VI) removal from aqueous solutions

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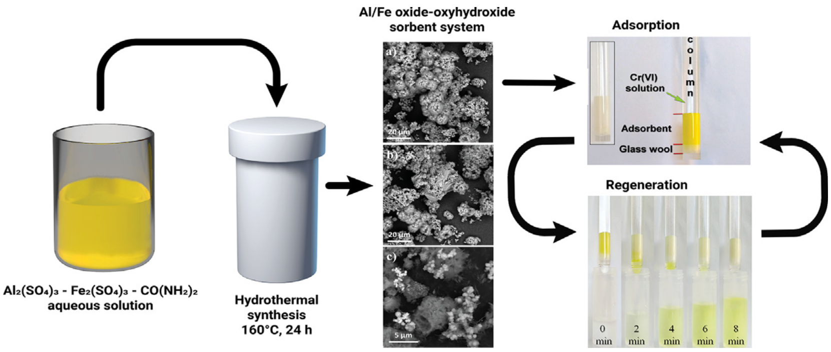
HIGHLIGHTS

- The Al/Fe oxide-oxyhydroxide composite powders were prepared by hydrothermal method.
- The composition, physicochemical and adsorption properties were investigated.
- Powders showed higher Cr(VI) adsorption capacity as compared to the world analogues.
- The possibility of regeneration and reuse of adsorbents is shown.
- Proposed adsorbent systems may find extensive applications in water treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Today, one of the most important global tasks is the treatment of waste water from various pollutants, including heavy metal. Adsorption is a promising method of wastewater treatment in terms of efficiency and cost. In this paper, the Al/Fe oxide-oxyhydroxide composite powders, prepared by hydrothermal method using metal sulfate solutions and urea as precursors, are investigated as adsorbents for chromium. The influence of the $[Al^{3+}]:[Fe^{3+}]$ ratio on the phase composition, textural properties, morphology, and thermal effects of composites was also investigated. It is shown that the maximum specific surface area ($190\,m^2/g$) is reached for samples synthesized from solutions with $[Al^{3+}]:[Fe^{3+}] = 1:0$ and 1:1. Cr(VI) adsorption from solutions was performed under static (batch adsorption) and dynamic (column adsorption) conditions. It is shown that the presence of sulfate ions on the surface of Al-containing samples suppresses the Cr(VI) adsorption. The maximum adsorption capacity in batch adsorption (3.66 mg/g) has a sample synthesized from solutions with $[Al^{3+}]:[Fe^{3+}] = 1:6$, which is characterized by a high (but not maximal) surface area ($102\,m^2/g$), a low content of sulfates and maximum zeta potential. Sorption experiments showed that the mean free adsorption energy is below 8 kJ/mol for all samples, indicating the adsorption process as the physical in nature and suggesting the possibility of Cr

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(VI) desorption and adsorbent regeneration. Based on the results of fixed-bed adsorption experiments, an atypical form of breakthrough curves is noted, as well as an increase in sorption capacity of about 4–5 times as compared with batch adsorption.

1. Introduction

The problem of pollution in general (and pollution of the waste water in particular) is one of the main problems of our time. The unclear drinking water is widely distributed, especially in western China, India, Bengal etc., because the groundwater usually contains high concentrations of toxic arsenic, chromium and lead etc [1]. Chromium mainly exists in nature in the derived form and can be in a trivalent Cr (III) or hexavalent Cr(VI) state. Compounds of Cr(VI) are common pollutants in natural waters, representing a serious threat to both the environment and human health. The maximum allowable emission standard of Cr(VI) on surface water according to World Health Organization guidelines [2] is 0.05 mg/L. The chromium compound exhibit pronounced carcinogenic effect [3] and ability to penetrate through the cell membrane and react with the intracellular material [4]. The structural similarity of chromates to physiological sulfates and phosphate ions enables molecular mimicry and easy entry of Cr(VI) into cells through nonspecific anion channels [5]. Toxic effects of chromium are respiratory problems, hemolysis, acute renal failure, weakened immune system, alteration of genetic material, lung cancer and pulmonary fibrosis [6]. The presence of chromium in the environment is a result of both anthropogenic (wood, leather industry, metallurgy, production of inorganic chemicals) and non-anthropogenic factors [7].

Since polluted water is a global environmental issue, some technologies to treat waste water have been developed, such as adsorption, ion-exchange, chemical coagulation or oxidation, electrodialysis, electrochemical reduction/precipitation, photocatalysis, and membrane filtration [8]. Among these methods, adsorption as a green technology [9] is considered to be one of the most promising strategies because of its relatively low-cost, simplicity of operation, and high separation efficiency [2,8,10–12]. Other methods suffer from drawbacks like high capital and operational cost and problems in disposal of the residual metal-containing sludge [13].

The key to applying the adsorption method is the fabrication of adsorbents. A suitable adsorbent should be stable, low-cost, environment-friendly, efficient to remove different contaminants, have high adsorption capacity and rate of adsorption, and have high selectivity for different concentrations [8,9,14]. To gather data, various conventional adsorbents, such as activated carbon, clay, polymers, metal oxides and silicon nanomaterials have been studied [8,15,16]. Many of these adsorbents have some deficiencies, including low adsorption capability, low recyclability, and high cost.

The rational structure design and facile synthesis of adsorbents always play critical roles in the adsorption technology [12]. Hydrothermal method is the most convenient and widely used for synthesis of nano- and microsized adsorbents with the desired properties due to the ability to control the temperature, vapor pressure and duration of the synthesis [17,18]. Much attention is paid to the study of adsorbents with a hierarchical structure [19].

Boehmite (γ-AlOOH) and alumina, as well as iron oxide, are widely used as an adsorbent and catalyst [20]. However, there have been several studies reporting that the mixed oxides of the metals showed better efficiency than many of the single metal oxides [21,22]. For example, a synergistic effect was observed by Gulshan et al. [23] for $H_2PO_4^-$ adsorption on Fe_2O_3/Al_2O_3 powders. It has been shown that the compositions have better uptake ability in contrast to pure samples, probably due to the structural stresses induced by incorporation of Al^{3+} ion in the iron oxide structures.

There is a number of works devoted to Cr(VI) adsorption on the surface of aluminum and iron oxyhydroxides [3,24]. So, Ajouyed et al. [3] studied the performances of removal of hexavalent chromium from aqueous solution by three different oxy-hydroxides: hematite, goethite and α-alumina. Results showed that the adsorption of Cr(VI) strongly depends on the pH, but is independent of ionic strength for hematite and goethite. Langmuir equation was found to fit the equilibrium data for Cr(VI) adsorption. Granados-Correa et al. [24] studied the adsorption behavior and the removal of Cr(VI) ions from aqueous solutions as a function of contact time, initial pH solution, amount of adsorbent and initial metal ion concentration, using batch technique. It was shown that adsorption equilibrium is attained within a short contact time, and the Cr(VI) adsorption was favored at higher temperatures and at slightly initial acid pH values in the equilibrium. The results indicate that boehmite is an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions, and it could be useful in the treatment processes of industrial wastes or for analytical applications.

Nevertheless, there is a limited number of studies dealing with hydrothermal synthesis and properties of the mixed oxides of aluminum and iron. Mahapatra et al. [25] synthesized mixed iron and aluminum oxide (Fe_2O_3–Al_2O_3) by hydrothermal method, which were further investigated as adsorbents for Congo red. It was shown that adsorption equilibrium is attained within a short contact time of 15 min, and the adsorption capacity was 498 mg/g. The aim of this study is to investigate the effect of the $[Al^{3+}]$:$[Fe^{3+}]$ ratio on the phase composition, textural characteristics, morphology, thermal effects, and Cr(VI) adsorption properties of the composite powders prepared by hydrothermal treatment of metal sulfate – urea solutions.

2. Experimental

2.1. Sample preparation

The procedure employed for preparing Al/Fe oxide–oxyhydroxide composite powders is described as follows. Firstly, $Al_2(SO_4)_3{\cdot}18H_2O$ (98 + %, ACROS Organics), $Fe_2(SO_4)_3{\cdot}9H_2O$ (97%, Sigma-Aldrich) with certain molar ratio (Table 1) and stoichiometric amount of urea (98.5%, Panreac) were dissolved in 60 mL of distilled water under magnetic stirring. The concentration of metal ions varied in the ranges of 0.16 ± 0.03 mol/L. The obtained solutions were transferred into Teflon-lined stainless steel autoclaves and treated at 160 °C for 24 h. After the reaction finished, the autoclave was naturally cooled down to room temperature. The solid products were collected by centrifugation (Ekros PE-6910 centrifuge, 3000 rpm, 30 min), washed with distilled water and dried at 50 °C in a ShS-0.25–45 drying chamber.

2.2. Adsorption experiments

Cr(VI) adsorption from solutions was performed under static (batch adsorption) and dynamic (column adsorption) conditions.

Table 1
The results of XRD analysis of powders.

Sample	$[Al^{3+}]$:$[Fe^{3+}]$	Phase content, vol%/Crystalline size, nm			
		γ-AlOOH	α-Fe_2O_3	α-FeOOH	$(H_3O)Al_3(SO_4)_2(OH)_6$
A1	1:0	60.3/8	–	–	40.7/55
A2	6:1	91.7/9	8.3/–	–	–
A3	1:1	28.5/13	71.5/27	–	–
A4	1:6	–	82.6/33	17.4/17	–
A5	0:1	–	90.4/43	9.6/14	–