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Immobilization, enrichment and recycling of Cr(VI) from wastewater using a red mud/carbon material to produce the valuable chromite ($FeCr_2O_4$)

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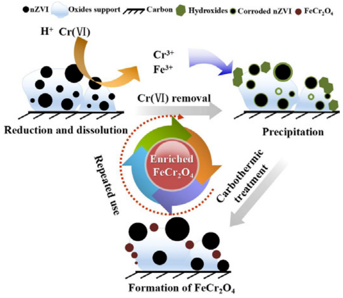
HIGHLIGHTS

- An inexpensive RM/carbon material with dispersed nZVI was prepared by carbothermal method.
- The material exhibited excellent removal efficiency of Cr(VI).
- The Cr(VI) can be immobilized and enriched by forming $FeCr_2O_4$ after carbothermal regeneration.
- The calcined ash with 45 wt% accumulated Cr_2O_3 can be recycled as the substitute for chromite ore.

GRAPHICAL ABSTRACT



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ABSTRACT

It is a long-term goal to develop an inexpensive, eco-friendly, and effective approach for the purification of wastewater containing heavy metal elements such as Cr(VI). In this study, a red mud (RM)/carbon material with dispersed nano zero-valent iron (nZVI) is fabricated to collect, immobilize, enrich, and recycle Cr(VI) from wastewater by repeatedly using the spent sample after carbothermal regeneration. The regenerated RM/carbon sample maintains an excellent removal efficiency of Cr(VI), and the collected Cr species can be firmly immobilized and gradually accumulated through forming highly stable chromite ($FeCr_2O_4$) with the assistance of carbothermal treatment. A detailed study of structure–function relationships reveals that Cr(VI) in wastewater is first reduced to Cr(III) by nZVI, and is then collected on RM/carbon in the form of Cr-Fe hydroxide species, which is converted to a stable $FeCr_2O_4$ phase immobilized on the regenerated RM/carbon by carbothermal treatment. Moreover, the repeated use/regeneration process facilitates the gradual growth, separation, and exposure of nZVI particles on the external surface of the RM/carbon, which improves its reaction activity with H^+ and Cr(VI). The elevated activity of nZVI as well as the high stability of the accumulated $FeCr_2O_4$ account for the excellent cycle efficiency of Cr(VI) removal. Nearly all of the nZVI (97.8%) in RM/carbon can be utilized to produce $FeCr_2O_4$ with more than 45 wt% Cr_2O_3 content in the final calcined ash, which can be recycled as a valuable substitute for natural chromite ore in the steel industry with no secondary pollution. The demonstrated superiority of the material and process offer promising technological, economic and environmental benefits for the simultaneous utilization of chromium wastewater and RM solid wastes.

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1. Introduction

The development of an inexpensive and effective approach for purifying polluted water containing heavy metals such as Cr(VI) without generating secondary pollution is one of the most arduous tasks in the field of water treatment [1–4]. Great progress has been made in terms of new technologies, various materials and economical preparation methods during the past ten years [5–8]. However, there are still great environmental risks associated with the potential secondary pollution sources (e.g., precipitated sludge, spent adsorbent, or eluted/concentrated wastewater) that may release collected heavy metal species [9]. The key to solve the problem is the permanent immobilization or recycling of these collected heavy metal elements [3,10]. Unfortunately, collected Cr species are not always stable enough to be considered harmless wastes; it is also technically/economically infeasible to separate and recycle collected Cr species without sufficient concentration. Therefore, the development of an environmentally-friendly and practical material/route for collecting, immobilizing, enriching, and recycling Cr(VI) from wastewater is highly desirable but is a great challenge.

Red mud (RM) is a solid waste residue with a huge increment and reserves from the digestion of bauxite ores with caustic soda during the production of alumina (Al_2O_3). It has caused serious environmental problems including land occupation, soil groundwater and contamination, and even marine pollution [11–13]. On the other hand, the rich components in RM such as Fe_2O_3, Al_2O_3 and SiO_2 may also be recycled as valuable resources, and hence the development of effective approach for utilizing this waste remains a long and arduous task [14,15]. Although simply treated RM is reported to have a good capacity for removing some heavy metal/semimetallic elements (e.g., Pb, Cd, As), it has a very poor removal capacity for Cr(VI) owing to its good stability across a wide pH range [16–20]. As an alternative, nano zero-valent iron (nZVI) materials have aroused intense research interest with their extraordinary performance in recent years, and new methods such as carbothermal synthesis have also been developed to improve the stability and dispersity of nZVI [21–26].

Inspired by these latest progresses, we explore the idea of fabricating RM/carbon materials by carbothermal treatment of mixed RM-coal powder as an inexpensive and effective agent for Cr(VI) removal. During this process Fe_2O_3 in RM is reduced to nZVI and the other components (Al_2O_3 and SiO_2 from the RM and residual carbon from the coal) act as dispersants and stabilizers of nZVI. The advantages of the presented material/method are attractive: the utilization of RM waste, low material cost, high activity of nZVI, and facile carbothermal regeneration of the spent sample.

Natural chromite ore ($FeCr_2O_4$) is a rare mineral and has important industrial applications such as steelmaking, production of chromium salts and refractory materials, and chromite with a content of Cr_2O_3 above 30 wt% is regarded as a high grade mineral resource. Interestingly, we discover the collected Cr species on the spent RM/carbon can be firmly immobilized and gradually accumulated in the form of highly stable chromite ($FeCr_2O_4$) phase after repeated use/carbothermal regeneration process, and the excellent efficiency of Cr(VI) removal can be still maintained even with only a small amount of nZVI left in the regenerated RM/carbon material. The accumulated content of Cr_2O_3 can reach above 45 wt% in the air-calcined ash of the final spent RM/carbon, which can be directly recycled as the valuable substitute for natural chromite ore in the steel industry with no secondary pollution. The demonstrated effective recycling of Cr(VI) using the cheap RM/carbon material to produce the valuable $FeCr_2O_4$ will provide a new possibility for the resource utilization of both chromium wastewater and RM solid waste.

2. Materials and methods

2.1. Materials

Raw RM and brown coal were from Shandong Aluminum Industry Company and Kumul Naomaohu, respectively. Brown coal was chosen as the carbon source because it is less costly. The samples were dried and ground before further utilization. Other chemicals including HNO_3, NaOH, and potassium dichromate were of reagent grade and used without any pretreatment.

2.2. The sample preparation

Raw RM was first treated using a previously reported acid–base neutralization method to remove sodium before use [27]. The obtained RM was then milled with brown coal (mass ratio of RM:coal = 1:2) to form a uniform powder. The pre-experiment proved that the carbothermal temperature had to reach 800 °C for the complete reduction of Fe_2O_3 to nZVI as shown in Fig. S15. Thus, the RM/carbon material was obtained by thermal treatment of the above powder under an N_2 atmosphere at 800 °C for 1 h. For comparison purposes, carbonized coal sample was also obtained by carbonization of the brown coal under an N_2 atmosphere at 800 °C for 1 h, and the H_2-reduced RM sample was prepared by reducing the RM with H_2 at 600 °C for 1 h. The spent RM/carbon material was regenerated by direct thermal treatment of the spent sample under an N_2 atmosphere at 800 °C for 1 h. To gain a deep insight into the effect of the regeneration times on the removal efficiency of Cr(VI), aged samples were prepared by heat treatment of the spent RM/carbon after ten cycles with a certain amount of $Cr(NO_3)_3$ (mass ratio of $Cr(NO_3)_3$/(RM/carbon) = 0.567 and 0.937, respectively) under an N_2 atmosphere at 800 °C for 5 h. As an extension study, the nZVI/activated carbon sample was also prepared by incipient impregnation of activated carbon in a ferric nitrate solution followed by carbothermal treatment under an N_2 atmosphere at 800 °C for 1 h.

2.3. The sample characterization

The chemical composition was determined using an Axios X-ray fluorescence (XRF) spectrometer (PANalytical X'pert, Almelo, Netherlands). X-ray diffraction (XRD) was performed in a 2θ range of 10° to 90° on a D/Max-RB diffractometer (Rigaku Corp., Tokyo, Japan) with Cu Kα radiation. Nitrogen adsorption/desorption isotherms were recorded on an ASAP 2020 (Micromeritics Instrument Corp., Norcross, USA) at 77 K. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (S_{BET}), and the pore size distributions were calculated from the adsorption branch using the Barret–Joyner–Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250Xi electron spectrometer from Thermo Fisher Scientific Corp. (New York, USA). The reported binding energy values are all corrected by referring to the binding energy of C 1 s, which is 284.8 eV. The morphology was observed using a JSM-7001F scanning electron microscope (SEM, JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 10 kV, and a JEM-2100 JEOL transmission electron microscope (TEM) at 200 kV. Energy dispersive spectrum (EDS) analysis was also executed during the SEM observation. Thermogravimetry (TG) measurements were carried out on an Exstar TG/DTA 7300 (Seiko Instrument Inc., Tokyo, Japan) under an air atmosphere at a heating rate of 5 $°C·min^{-1}$ from 30 °C to 1000 °C. The concentrations of Cr and Fe ions in solution were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, iCAP 6300, Thermo Scientific Corporation, USA). The value of Cr(III) concentration was calculated by simultaneously detecting the total Cr(VI)/Cr(III) concentration and the single Cr(VI) concentration through ICP and the 1,5-diphenyl carbazide method [28], respectively.