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Nanoscale zero-valent iron particles modified on reduced graphene oxides using a plasma technique for Cd(II) removal

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ABSTRACT

Nanoscale zero-valent iron particles supported on reduced graphene oxides (NZVI/rGOs) from spent graphene oxide (GO)-bound iron ions were developed by using a plasma reduction method to improve the reactivity and stability of NZVI. The specific surface area (SSA) of NZVI/rGOs was 117.97 $m^2\ g^{-1}$, while the SSA of NZVI particles was 59.59 $m^2\ g^{-1}$. The adsorption kinetics was quite fast, which could be completed within 50 min. The adsorption capacity of NZVI/rGOs toward Cd(II) was 425.72 mg g^{-1}, which was higher than other adsorbent materials. Moreover, the NZVI/rGOs could be regenerated by the plasma reduction technique and maintained high removal performance after four cycles. NZVI/rGOs also showed high removal capability toward Cd(II) in the simulated Cd(II)-bearing effluent. The above experimental results show that the NZVI/rGO can be efficient materials for the purification of Cd(II)-contaminated water in the environmental pollution management.

1. Introduction

Heavy metal pollution has become a worldwide environmental concern, and wastewater containing heavy metal ions becomes the main source of water contamination [1]. Cadmium (Cd) was regarded as an extremely toxic metal [2], and was classified as the priority pollutant by the Department of Environment, UK [3] and Dangerous Substance Directive in European Economic Community. Cd has also been included as group B1 carcinogen by US Environment Protection Agency [4]. The guideline value for Cd in drinking water recommended by World Health Organization is 0.005 mg L^{-1} [5]. It is of great significance to develop advanced technologies and superior materials for the removal of Cd from aquatic environments.

Using low cost, green and high adsorbent nanoparticles are good approach to remove pollutants [6–9]. Nanoscale zero-valent iron (NZVI) particles have been considered as one of the most promising permeable barrier materials applied in the groundwater purification and wastewater treatment because of the large specific surface area, extremely small particle size, excellent in-situ reactivity and high injectability into aqueous solution [10–12]. Much attention has extensively been focused on NZVI particles for the rapid removal of metal ions [13–18]. However, some technical issues such as the agglomeration, bad stability, and shortage of durability and mechanical strength [19,20], hinder the practical application of NZVI particles. Furthermore, the aggregation is hard to be avoided due to the magnetic interaction among NZVI particles. Researchers have reported that the aggregation of NZVI particles can be reduced when they were supported on substrates. In addition, their dispersion ability and specific surface area (SSA) were also improved, and thus their reactivity was enhanced [21,22].

NZVI particles supported on graphene not only increased the dispersion ability and stability but also strengthened electron transfer and preconcentration of pollutants by coupling the advantages of NZVI reactivity and graphene adsorption ability [23–31]. NZVI particles decorated graphene sheets by chemical reaction increased SSA and Cr(VI) removal capacity compared to bare NZVI particles [32]. Reduced GOs (rGOs)-Fe(0)-Fe_3O_4 synthesized by thermal annealing in a H_2/Ar atmosphere was reported for the retention of heavy metal ions with high surface area and high efficiency [33].

GOs can be used for Fe ion removal from aqueous solutions. If GO-bound Fe ions was pushed away as waste after adsorption, which not only increases cost but also produces secondary pollution. For the realization of environmental protection, a new design concept to achieve regeneration and utilization of such GO-bound Fe ions should be introduced. From this point of view, spent GO-bound Fe ions was reused to prepare NZVI particles supported on reduced GOs (denoted as NZVI/rGOs) by a H_2/Ar plasma reduction technique. The

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plasma-assisted technique has been widely used in advanced technologies for manufacturing a large number of products, *e.g.*, plastic bags, automobile bumpers, airplane turbine blades, artificial joints, and microelectronics [34]. In the plasma process, samples are exposed to physical bombardment and/or chemical reactions caused by reactive radicals and energetic particles. These chemical and physical actions allow its application in surface modification and material synthesis [35]. Exposure to H_2/Ar gas plasma may remove the oxygen-containing functional groups by hydrogen radicals, and the content of hydrogen radicals can also be enhanced by argon due to penning ionization [36]. Plasma method showed superior advantages to conventional approaches, such as thermal annealing, electrochemical reduction, chemical and thermal techniques, due to the low temperature, environmentally friendly process and short time for the reaction.

In this work, the NZVI/rGOs were prepared by using H_2/Ar plasma reduction method, and were applied for removing Cd(II) from aqueous solution. In addition, the NZVI/rGOs could also be regenerated by using this plasma technique. The mechanisms of Cd(II) removal by NZVI/rGOs were discussed by using X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental details

2.1. Preparation of NZVI/rGOs

GOs were synthesized by using the modified Hummers method [25]. Then a desired amount of GOs was dispersed in Milli-Q water by ultrasonication for 30 min. A certain amount of Fe(III) solution (mass ratio of Fe(III)/GOs = 1:4) was added to the GO suspension. The suspension was stirred for 12 h to achieve adsorption equilibrium. The presence of oxygen-containing functional groups on the GOs allowed the Fe species to be adsorbed [37]. After adsorption, the solution was centrifuged at 8000 rpm for 10 min to remove the residual Fe(III) ions. The solvent was changed to ethanol, and the suspension was centrifuged again under the same conditions. Finally, the supernatant was replaced by fresh ethanol. The material was filtered through a membrane filter (0.2 µm, Whatman). Then obtained materials were placed in the experimental setup, which consisted of a discharge chamber, plasma discharge device and vacuum system. NZVI/rGOs were synthesized using H_2/Ar plasma technique at 4.7 Pa pressure, 80 W charge power, 2:1 gas flow rate ratio of H_2 to Ar, and 30 min treatment time. As a comparison, NZVI/rGOs with Fe(III)/GO mass ratios of 1:1, 1:4 and 1:5 were prepared by the same procedure and were denoted as NZVI/rGOs (1:1), NZVI/rGOs (1:4) and NZVI/rGOs (1:5), respectively. The characterization methods of NZVI/rGOs were shown in Supplementary material.

2.2. Adsorption experiments

Cd(II) adsorption was carried out by batch adsorption experiments at room temperature, where suspensions of the NZVI/rGOs, NZVI particles and rGO, stock solutions of $NaNO_3$ and Cd(II) were added to achieve the desired concentrations of the different components. The desired pH was achieved by injecting negligible volumes of 0.01 or 0.1 mol L^{-1} HNO_3 or NaOH. The ionic strength of the background electrolyte was fixed at 0.01 mol L^{-1} $NaNO_3$. At different adsorption time intervals, the solid and liquid phases were magnetically separated using a hand-held magnet. Cd(II) concentrations were measured using a Shimadzu 6300 atomic absorption spectrophotometer. The amount of adsorbed Cd(II) was calculated as the difference between the initial concentration (C_0) and the equilibrium one (C_e) in the supernatant (removal (%) = (C_0-C_e)/$C_0 \times 100$). All of the experiments were conducted in triplicate, and the error values were less than 5%. The regeneration experiments were shown in Supplementary material.

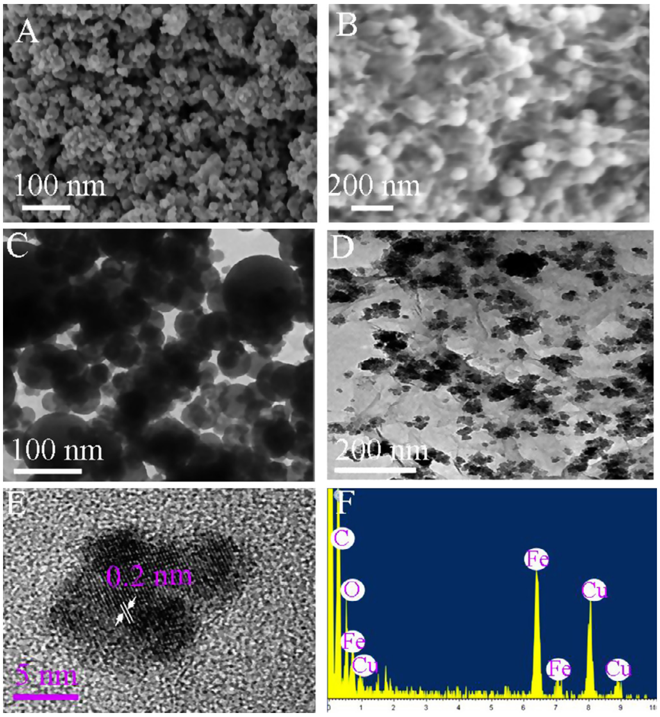

Fig. 1. SEM images of NZVI particles (A) and NZVI/rGOs (1:4) (B); TEM images of the NZVI particles (A) and NZVI/rGOs (1:4) (B); HRTEM of NZVI/rGOs (1:4) (C) and the corresponding EDS pattern (D).

3. Results and discussion

3.1. Characteristics of NZVI/rGOs

The morphologies of the NZVI particles and NZVI/rGOs were characterized by using SEM, TEM and HRTEM. Fig. 1A shows that the NZVI particles aggregated together tightly and formed a bunch-like structure, whereas the NZVI particles loaded on rGOs appeared in a finely dispersed state (Fig. 1B). Fig. 1C showed that the NZVI particles were aggregated together tightly and the core-shell structure consisting of a core layer of Fe(0) and a shell layer of iron oxides was observed obviously, while the NZVI particles loaded on rGOs dispersed homogeneously (Fig. 1D). Fig. 1D showed that NZVI particles were loaded on the rGO and the particle size was approximately 40 nm. These observations implied that rGOs reduced NZVI aggregation. Fig. 1E showed the NZVI particles were not simply mixed up or blended with rGOs, rather, they were embedded inside the rGO sheets. Clear lattice fringes suggested the formation of crystalline iron nanoparticles in the NZVI/rGOs. The interplanar distance between the fringes was 0.2 nm, which was relevant to the (110) plane of body-centered cubic (bcc) iron [33]. The EDS spectrum shown in Fig. 1F demonstrated the existence of C, O and Fe.

The XRD patterns of the rGOs, NZVI particles and NZVI/rGOs (1:4) are shown in Fig. 2A. The intense diffraction peaks at 2θ of 99.2°, 82.2°, 65.1° and 44.7° corresponded to the (220), (211), (200) and (110) planes [38] and were consistent with the standard XRD data for body-centered cubic (bcc) Fe(0) (JCPDS No. 87–0722), suggesting that rGO sheets were covered by the NZVI particles. The presence of amorphous iron^{III} oxide/hydroxide, magnetite (Fe_3O_4) and/or maghemite (γ-Fe_2O_3) and lepidocrocite (γ-FeOOH) with weak intensity in the XRD patterns of the NZVI particles was due to the surface oxidation of NZVI particles. These bands were not observed for the sample of NZVI/rGOs, indicating that the rGO sheets could prevent NZVI particles from quick surface oxidation. The rGOs showed a broad peak at