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Enhanced removal of chromate by graphene-based sulfate and chloride green rust nanocomposites

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ABSTRACT

Green rust, a double layered (Fe^{II}, Fe^{III}) hydroxide, can impact the mobility and toxicity of highly reactive contaminants such as chromate through reduction of Cr^{VI} to Cr^{III}. The reduction of Cr^{VI} by sulfate and chloride green rusts (GRs) was comparatively studied for a range of initial Cr^{VI} concentrations and pH values. At an equal molar ratio of Cr^{VI} to Fe^{II} in GR, sulfate green rust ($GRSO_4$) removed higher amounts of Cr^{VI} from solution than chloride green rust (GRCl). The rate of the reactions with respect to initial concentration of Cr^{VI} is well described by pseudo-second order model. The GRCl reacted with chromate much faster than $GRSO_4$. The obtained pseudo-second order rate coefficients for the GRCl and $GRSO_4$ ranged from 99.53 to 14.24 and 35.45 to 4.53 mmol/s, respectively. Graphene-based green rust nanocomposites were prepared using partially reduced graphene (PRG) and examined for removal of Cr^{VI}. The efficiency of Cr^{VI} removal by $GRSO_4$/PRG and GRCl/PRG nanocomposites was dependent on the mass ratio of PRG to total Fe precipitated as GR (PRG:$Fe_{(s)}$) and the highest removal was observed at PRG:$Fe_{(s)}$ mass ratios of 1:2. In comparison with bare GRs, the GR/PRG nanocomposites removed higher amounts of Cr^{VI} from solution. However, the reduction rates of Cr^{VI} by GR/PRG nanocomposites were ~2 to 3-fold lower than those observed by bare GRs in both sulfate and chloride systems.

1. Introduction

Green rusts (GRs) are layered double (Fe^{II}, Fe^{III}) hydroxides that belong to sjögrenite–pyroaurite mineral class with the general formula of $Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2[A^{n-}]$. mH_2O, where x is the molar fraction of Fe^{III}, A^{n-} donates the intercalated anion (mainly $SO_4{}^{2-}$, $CO_3{}^{2-}$ and Cl^-) and m is varying amount of interlayer water [1]. Trioctahedral layers of $Fe(OH)_2$ are positively charged due to isomorphic substitution of Fe^{III} for Fe^{II}, which is neutralized by hydrated anions in the interlayer. Specifically the ideal compositions of $GRSO_4$, $GRCO_3$ and GRCl are respectively $[Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}\ SO_4.\ 8H_2O]$, $[Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}\ CO_3.\ 8H_2O]$ and $[Fe^{II}{}_3Fe^{III}{}_1(OH)_8\ Cl.\ 2H_2O]$ [2].

Due to their large active surface and interlayer which exchanges anions, GRs act as potentially strong sorbents [3]. In addition, the structural Fe^{II} makes GRs as strong reductants of many organic (*e.g.*, trichloroethen) and inorganic (*e.g.*, $CrO_4{}^{-2}$, $NO_3{}^-$) pollutants [4–6].

Hexavalent chromium (Cr^{VI}) is a potent carcinogen substance and highly toxic for living organisms. In contrast with Cr^{VI}, Cr^{III} is less toxic and readily sorbs to the soil particles and in natural to alkaline environments precipitates as Cr^{III} hydroxides or chromium-iron hydroxides $(Cr_xFe_{1-x})(OH)_3$ when dissolved Fe is present [7,8]. Reduction of Cr^{VI} to Cr^{III} in the presence of both aqueous [7,9] and solid-bound [10,11] Fe^{II} is a rapid process combined of both heterogeneous and homogenous reactions and can be described by Eq. (1).

$$Cr^{VI} + 3Fe^{II} = Cr^{III} + 3Fe^{III} \quad (1)$$

Bond and Fendorf [12] investigated the reduction rates of Cr^{VI} by $GRSO_4$, GRCl and $GRCO_3$ at pH 7 and found that the kinetics of the reaction for all three can be described with pseudo-first order kinetic with respect to Cr^{VI} concentration. However, Bond and Fendorf [12] used mass basis concentration for comparison of rates between GRs and did not account the differences in Fe^{II} content in these three phases. They found that reduction rates of Cr^{VI} by GRCl is approximately two times faster than those of $GRSO_4$ and $GRCO_3$ which could be a result of combined effect of higher external surface area and Fe^{II}/Fe^{III} ration in GRCl. In a similar study, Hansen et al. [6] examined reduction kinetics of nitrate

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by $GRSO_4$ and GRCl, and obtained that reduction rate of nitrate to ammonium by GRCl follows first-order kinetic with respect to Fe^{II} and is 30–40 times faster than the rate observed by $GRSO_4$. Furthermore, Hansen et al. [6] stated that high rate of nitrate reduction by GRCl was related to ready exchange of chloride with nitrate in the interlayer and high content of Fe^{II} in GRCl structure.

The first aim of this article was evaluating the reactivity of $GRSO_4$ and GRCl on chromate reduction affected by various experimental conditions. We used the ratio of the number of moles of Cr^{VI} added to the GR suspension (nCr^{VI}) to the number of moles of Fe^{II} present in GR ($nFe^{II}_{(s)}$) for all Cr^{VI} removal experiments. This parameter provides a precise comparison between $GRSO_4$ and GRCl reactivity and will lead to the authentic conclusions. The next goal of this study was to prepare graphene-based/GRs nanocomposites and compare their efficiency with the bare GRs on removal of Cr^{VI}. In this study, we used partially reduced graphene oxide (PRG) as supporting media instead of GO or completely reduced GO (RGO) to prepare the nanocomposites. The surface of GO is highly negatively charged [13], which is not favored in removal of anionic pollutants, as electrostatic repulsion from negatively charged functional groups will be limiting. On the other hand, completely reduced GO is a non-polar hydrophobic substance with low affinity for adsorption of polar species and high tendency for agglomeration. So we used PRG with the goals of (1) overcoming the charge repulsion between negatively charged chromate ions and GO surface, (2) providing acceptable solubility in water and electrical conductivity of graphene and (3) partially maintaining functional groups of GO surface for attachment of external Fe species. These objectives were accomplished by using sodium borohydride as a moderate reductant of GO [14].

2. Materials and methods

2.1. Preparation of $GRSO_4$ and GRCl

Synthesis of GRs was carried out by co-precipitation method [15,16] inside a 1 l glass reactor with inlets for nitrogen gas, pH electrode, NaOH solution and sampling port. All solutions were prepared using deoxygenated distilled water. Briefly, 10 ml of NaOH solution (0.5 M) was added to a 40 ml mixed solution of Fe^{II} (as $FeSO_4$. $7H_2O$) and Fe^{III} (as $Fe_2(SO_4)_3$. $6H_2O$) with the total concentration of 0.05 M ($x = 0.33$, $nOH{:}nFe = 2{:}1$) under vigorous stirring with magnetic stirrer until complete $GRSO_4$ formation. The rate of NaOH addition was 100 µl/min. Similarly, the GRCl preparation was performed by dropwise addition of 0.5 M NaOH solution to the 0.05 M Fe solution ($FeCl_2$. $4H_2O$ and $FeCl_3$.$6H_2O$). The molar fraction of Fe^{III} and the nOH:nFe ratio in the initial solution were 0.25 and 2:1, respectively. During base addition to Fe solution, the pH was monitored. The final pH of resulting suspension was maintained at 7.5 ± 0.2 for both sulfate and chloride systems. In this study, all chemicals used were analytical-grade (purity > 97%).

2.2. Preparation of $GRSO_4$/PRG and GRCl/PRG nanocomposites

GO was synthesized via chemical oxidation of natural graphite powder according to the modified Hummers method [17]. The approach for GR/PRG nanocomposites preparation involved formation of GR nanosheets in the presence of PRG and then growing on the surface of PRG. GO was partially reduced by sodium borohydride and preparation of GRs was proceeded by assembling the Fe^{II} and Fe^{III} cations on the PRG nanosheets. This approach belongs to the *in situ* technologies for preparation of graphene-inorganic nanocomposites [18]. To prepare PRG, GO was treated with different concentrations of sodium borohydride ($NaBH_4$) (0.2, 0.3 and 0.5 M). 0.3 g of dried GO was introduced to 100 ml distilled water and the resulting suspension was sonicated for 1 h (30 kHz). Dispersed suspension of GO was diluted to 300 ml using distilled water and then 50 ml $NaBH_4$ solution was added to the suspension. The mixture was then stirred vigorously for 4 h. The suspension was filtered and washed several times with distilled water to remove the excess of reductant. Finally, resulting solid was dried at 75 °C.

Nanocomposites were prepared in the reactor used for the synthesis of GRs. In this study, GR/PRG nanocomposites were prepared with three different PRG:$Fe_{(s)}$ mass ratios of 1:1, 1:2 and 1:4, labeled as GR/PRG_1, GR/$PRG_{0.5}$ and GR/$PRG_{0.25}$, respectively. $Fe_{(s)}$ represents the mass concentration of total Fe precipitated as GR. Briefly, certain amount of PRG powder was added to 40 ml distilled water and sonicated for 15 min. The ferric and ferrous iron salts were added to the suspension and stirred well for 10 min. Thereafter, suspension was titrated with 0.5 M NaOH to form GR/PRG nanocomposites. Nanocomposites were prepared with the same molar fraction of Fe^{III} and nOH/$Fe_{(s)}$ ratio described for preparation of GRs.

2.3. Characterization methods

X-ray diffraction (XRD) patterns of the samples were recorded using Siemens (Germany) powder X-ray diffractometer with Cu-kα radiation at 40 keV and emission current of 30 mA. GR samples for XRD analysis were prepared in nitrogen atmosphere by admixing with glycerol to limit oxidation during analysis. Formed paste was smeared onto the sample slide and analyzed at 4–40 2θ. Fourier transform infrared (FTIR) spectra of GO and PRG were recorded using a Tensor 27 (Germany) spectrometer with potassium bromide (KBr) pellets. Scanning electron microscopy (SEM) was performed on a Mira3-Tescan at an accelerating voltage of 20 kV to examine the size and morphology of bare GRs and nanocomposites. For SEM imaging filtered samples were vacuum-dried and loaded onto carbon stubs in nitrogen atmosphere and coated with gold in a vacuum deposition chamber. During transfer of samples into the instrument, the air oxidation was minimal as no change in the samples color was observed even in the GRCl, as a highly sensitive sample.

To determine the concentration of Fe^{II} in GRs, the filtered solids were dissolved in concentrated hydrochloridric (in the case of $GRSO_4$) or sulfuric (in the case of GRCl) acid (pH–3). Unfiltered samples were also dissolved by acidification and the aqueous Fe^{II} was measured to estimate the amount of Fe^{II} remained in supernatant by mass balance. Fe^{II} concentration was determined colorimetrically with 1,10-phenanthroline method [19]. Samples were immediately mixed with 1,10-phenenthroline and buffered around pH 5 with sodium acetate buffer solution (20%). Fe^{II} concentration was measured at 510 nm using a UV/Vis spectrophotometer (UV-9200, China). Sulfate and chloride ions were determined using turbidimetry and $AgNO_3$ titration methods, respectively [20,21].

In this study, we used freshly synthesized GR suspension in all experiments. Washing and drying of the samples were avoided to minimize the risk of oxidation and change in composition of GRs. To determine the quantity of solid in suspension, accurate volume of a set of suspension aliquots was measured and weighted after drying under vacuum.

2.4. Cr^{VI} reduction experiments

All batch experiments were carried out under N_2 gas flow in the same four-neck 1 l reactor used for GRs synthesis. 200 ml of potassium chromate (K_2CrO_4) solution with different concentrations was added to the reactor containing 50 ml of GR suspension to produce different Cr^{VI}/$Fe^{II}_{(s)}$ ratios of 0.3 (stoichiometric ratio), 0.6 and 0.9. Resulting slurry was magnetically stirred and at various time points 2 ml sample was taken for determination of

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