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Superior coagulation of graphene oxides on nanoscale layered double hydroxides and layered double oxides☆

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ABSTRACT

With the development and application of graphene oxides (GO), the potential toxicity and environmental behavior of GO has become one of the most forefront environmental problems. Herein, a novel nanoscale layered double hydroxides (glycerinum-modified nanocrystallined Mg/Al layered double hydroxides, LDH-Gl), layered double oxides (calcined LDH-Gl, LDO-Gl) and metallic oxide (TiO_2) were synthesized and applied as superior coagulants for the efficient removal of GO from aqueous solutions. Coagulation of GO as a function of coagulant contents, pH, ionic strength, GO contents, temperature and co-existing ions were studied and compared, and the results showed that the maximum coagulation capacities of GO were LDO-Gl (448.3 mg g^{-1}) > TiO_2 (365.7 mg g^{-1}) > LDH-Gl (339.1 mg g^{-1}) at pH 5.5, which were significantly higher than those of bentonite, Al_2O_3, $CaCl_2$ or other natural materials due to their stronger reaction active and interfacial effect. The presence of SO_3^{2-} and HCO_3^- inhibited the coagulation of GO on LDH-Gl and LDO-Gl significantly, while other cations (K^+, Mg^{2+}, Ca^{2+}, Ni^{2+}, Al^{3+}) or anion (Cl^-) had slightly effect on GO coagulation. The interaction mechanism of GO coagulation on LDO-Gl and TiO_2 might due to the electrostatic interactions and strong surface complexation, while the main driving force of GO coagulation on LDH-Gl might be attributed to electrostatic interaction and hydrogen bond, which were further evidenced by TEM, SEM, FT-IR and XRD analysis. The results of natural environmental simulation showed that LDO-Gl, TiO_2 or other kinds of natural metallic oxides could be superior coagulants for the efficient elimination of GO or other toxic nanomaterials from aqueous solutions in real environmental pollution cleanup.

1. Introduction

Recently, with the rapid development of nanomaterials and nanotechnology, many novel nanomaterials have attracted tremendous interests due to their multifunctional application, superior physicochemical property, large specific surface area and transferable electronic structure (Valente et al., 2009; Xiong et al., 2014; Yang et al., 2013). Interestingly, metallic-family materials, graphene-family materials and mineral-family materials have been the frontier and spotlight fields due to their unique microstructure and special performance (Ren et al., 2014; Wang et al., 2014a; Zaghouane-Boudiaf et al., 2012). Among these excellent materials, graphene, a layer two-dimensional graphite structure with atomic thickness (Sun et al., 2012; Zhao et al., 2012a), has been applied in various fields, such as energy storage devices (Yang et al., 2012), photocatalysis (Liu et al., 2016), sensors (Zhang et al., 2011a), battery component (Zhao et al., 2014) and effective adsorbent (Zhao et al., 2011, 2012b, 2013b) because of its unique electrical property, optical property, catalytic performance and adsorption capacity (Sun et al., 2012; Zhao et al., 2012a). Graphene oxide (GO), a

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typical derivatives and oxidation state of graphene, contains abundant oxygen-containing functional groups and active sites on its basal planes and edges (Yang et al., 2013; Zou et al., 2016). To date, GO has been a superior nanomaterial for potential applications in environmental remediation, energy storage, nanoscale batteries and liquid phase catalysis, etc., via the oxidation process to increase the oxygen-containing functional groups and to provide abundant active sites for polymerization and hybridization with other matrices (Jin et al., 2015; Zhao et al., 2013b). According to the literature survey (Jin et al., 2015; Wang et al., 2016; Zhao et al., 2012a; 2013c; Zou et al., 2016), the interaction of GO with other molecules (organic or inorganic materials) was mainly dominated by hydrogen bond, van der Waals interaction, π-π interaction and electrostatic interaction.

However, along with the widespread utilization of GO and GO-based nanocomposites, a new environmental issue has been realized and considered by many researchers. The potential toxicity and high mobility of GO can cause serious long-term cumulative toxic effect in livings, and it has been demonstrated that GO and its derivatives can accumulate in the lung, liver and spleen for long time (Li et al., 2015; Liao et al., 2011; Mao et al., 2013; Wen et al., 2015). Unlike organic pollutants, GO is not easily converted into harmless-end products or degraded to non-toxic small molecules, which tends to aggregate in living organisms with strong van der Waals (Seabra et al., 2014; Wen et al., 2015). Therefore, exploring an effective method to remove or to solidify GO and its derivatives from aqueous solutions has been an important and urgent problem for human beings and environmental pollution cleanup. At the same time, understanding the environmental behavior of GO in nature environment is crucial to evaluate potential danger and recycle underused GO or other nanomaterials.

During the past decade, many novel technologies have been applied to deal with various pollutants (e.g., organic dyes and heavy metal ions), such as ion exchange (Hu et al., 2014a,b), adsorption (You et al., 2002; Yuan et al., 2013; Zaghouane-Boudiaf et al., 2012), coagulation (Wang et al., 2016; Zou et al., 2016), chemical precipitation (Meunier et al., 2006) and membrane separation (Hu et al., 2014a,b; Zhang et al., 2012). Compared with these unique technologies, coagulation has been considered as a promising and potential method for the removal and aggregation of GO or other nanomaterials (Ren et al., 2014; Zou et al., 2016). For instance, Mg/Al layered double hydroxides (LDH) showed great coagulation capacities to GO from aqueous solutions, and the coagulation process was controlled by electrostatic interactions and hydrogen bonds, which was attributed to the abundant oxygen-containing functional groups on LDH surfaces (Wang et al., 2016; Zou et al., 2016). Therefore, the addition of an effective coagulant can decrease the migration and increase the aggregation of GO in aqueous solutions, which is useful for the remediation of GO in environmental cleanup.

As a kind of 2D anionic clay with a general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ (M^{II} and M^{III} represent divalent and trivalent metal cation, respectively, such as Mg^{2+}, Ni^{2+}, Ca^{2+}, Zn^{2+} and Al^{3+}, A^{n-} is an interlayer anion (e.g., Cl^-, SO_4^{2-} and CO_3^{2-}), x is defined as the ratio of $M^{3+}/(M^{2+} + M^{3+})$) (Wen et al., 2013; Wu et al., 2013), LDH materials have been applied as superior adsorbents, ion-exchangers and photocatalysis for various targets in environmental remediation and catalyze fields (Huang et al., 2015; Peng et al., 2014; Valente et al., 2009). Due to the unique microstructure and exchangeable interlayer ions, LDH is an important matrix and can combine with other nanomaterials. For instance, surface modified, calcined and anion intercalated LDHs have been used as multifunctional materials for the environmental cleanup (Shan et al., 2014; Wen et al., 2013; Zaghouane-Boudiaf et al., 2012). Calcined LDH (Layered Double Oxide, defined as LDO), as mixed metal oxide, possesses excellent layered structure and provides more active sites than the pristine LDH (Yuan et al., 2013; Zaghouane-Boudiaf et al., 2012). Furthermore, LDO exhibits superior adsorption capacity for organic and inorganic pollutants from aqueous solutions (Zaghouane-Boudiaf et al., 2012). Similarly, titanium dioxide (TiO_2) has extensive application in energy conversion and environmental pollutant cleanup, due to its abundance, environmental-friendly, and good environmental stability (Zhao et al., 2012a; 2013a; 2013c). With the emerge of metal matrix composites, LDO and TiO_2 as traditional metallic-family materials, can improve the surface charge and specific area through the binding with GO, and formed high performance graphene-metallic composites (Zhao et al., 2013c). Many research results have indicated that LDO and TiO_2 showed great adhesion with nanomaterials, especially for graphene and GO (Liu et al., 2016; Yuan et al., 2013; Zou et al., 2016). However, the interaction mechanism and coagulation behavior of GO and these materials is still scarce.

Herein, glycerinum-modified nanocrystallined Mg/Al layered double hydroxides (defined as LDH-Gl), calcined LDH-Gl (defined as LDO-Gl) and TiO_2 were synthesized with a facial hydrothermal process and used as effective coagulants for the coagulation of GO from wastewater and natural water. The objectives of this study were (1) to investigate the effect of coagulant dosage, solution pH, ionic strength, contact time, temperature and various anions or cations on GO coagulation on the three coagulants; (2) to study the interaction mechanism between GO and LDH-Gl, LDO-Gl and TiO_2 by SEM, TEM, FT-IR and XRD analysis; (3) to compare the coagulation of GO on various coagulants by qualitative analysis and batch experiments; (4) to explore the coagulation behavior of GO on natural materials in natural water system (reservoir). It is a highlight to compare the coagulation behavior of GO on metallic-family materials and mineral-family materials in natural water system.

2. Material and methods

2.1. Materials

The GO nanosheets were synthesized by modified chemical exfoliation of natural flake graphite (40 μm, 99.95% purity) (Zhao et al., 2012c, 2013c; Zou et al., 2016). Similarly, concentrated H_2SO_4, sodium nitrate ($NaNO_3$) and $KMnO_4$ were used to exfoliate flake graphite, and H_2O_2 (30 wt%) was applied to eliminate the excess MnO_4^- anions from suspension. LDH-Gl was prepared through chemical modification of inexpensive urea by a hydrothermal treatment process, and LDO-Gl was obtained by high-temperature calcination of as-prepared LDH-Gl. More detailed synthetic processes were described in supporting information (SI).

All reagents were of analytic purity and used without any further purification. Magnesium nitrate hexahydrate ($Mg(NO_3)_2\cdot 6H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_2\cdot 9H_2O$), titanium dioxide (TiO_2), glycerinum, urea (>99.5%), sodium chloride (NaCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), natural chlorides (e.g., $ZnCl_2$, $MgCl_2$, $NiCl_2$, $CaCl_2$ and $AlCl_3$), oxides (e.g., ZnO, Al_2O_3, MgO, CuO and Fe_2O_3) and clays mineral (e.g., amargosite, zeolite, Ca-montmorillonite, bentonite and diatomite) materials were purchased from Sinopharm Chemical Reagent Co., Ltd. Natural water was obtained from reservoir of NCEPU. Milli-Q water (18.2 MΩ cm^{-1}) was applied for all the experiments.

2.2. Characterization

The microstructure and morphology of the as-prepared coagulants were characterized by transmission electron microscopy