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Flocculation performance and mechanism of graphene oxide for removal of various contaminants from water

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ABSTRACT

The application of nanomaterials in water treatment plants has attracted significant attention recently. This study investigates the possibility of using graphene oxide (GO) as a novel flocculant to remove contaminants with different surface charges from water, including two particulate ones (kaolin and hematite) and two soluble ones (humic acid (HA) and cationic light yellow 7GL dye (7GL)). The flocculation performances of traditional polyaluminum chloride (PAC) and original graphite were also tested for comparison. Fractal theory was applied to evaluate the floc properties and explore the flocculation mechanism in combination with zeta potential measurements. For negatively charged contaminants, kaolin and HA, GO was observed to remove these contaminants successfully via the sweeping flocculation effect under acidic and neutral conditions. However, GO was less efficient than PAC. For positively charged contaminants, hematite and 7GL, the flocculation performances of GO were significantly improved than those of PAC via patching effect for hematite suspension and charge neutralization effect for 7GL solution. The results highlighted the extensive potential applicability of GO as a suitable flocculant in water treatment.

1. Introduction

Flocculation, which is widely applied because of its high efficiency and facile operation, is one of the most important industrial processes for water pretreatment (Yang et al., 2012c). The choice of flocculants during a flocculation process is significant to the final performance (Simate et al., 2012; Yang et al., 2011b; 2012c). At present, inorganic metal-based flocculants and synthetic polymeric ones are two of the most extensively applied flocculants. However, the increased concentration of metal ions of inorganic flocculants or noxious monomers in synthetic ones when these chemicals are used may have unwelcome implications to both related ecosystem and human health (Simate et al., 2012; Yang et al., 2011b). Although these problems can be reduced in a well performed water treatment process, novel environmentally friendly flocculants are still urgently needed due to higher requirements on water quality and economic reasons.

The rapid development of nanomaterials, which has advantages of large surface areas and more activated functionalized sites, brings an alternative way for water purification (Simate et al., 2012; Zhao et al., 2011a). Carbon-based nanomaterials are the most known because of their numerous unique advantages, and considerable studies (Belloni et al., 2009; Carabineiro et al., 2011; Chen et al., 2007; Hyung et al., 2007; Khaydarov et al., 2010; Ramesha et al., 2011; Simate et al., 2012; Sun et al., 2012; Yang et al., 2011a; 2012a; Zhao et al., 2011a,b; Zhu et al., 2012) have focused on these materials in water treatment. For example, carbon nanotubes (CNTs) have recently been found as effective adsorbents (Carabineiro

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et al., 2011; Chen et al., 2007; Gupta et al., 2011; Joseph et al., 2011; Yang et al., 2011a; Zhang et al., 2011b) and flocculants (Simate et al., 2012). Compared with one-dimensional CNTs, two-dimensional (2D) graphene-based materials, with atomic thickness and relatively larger surface area, are more fascinating (Novoselov et al., 2004; Yang et al., 2012a; Zhao et al., 2011a,b). One significant branch of graphene-based materials is graphene oxide (GO) (Ramesha et al., 2011; Sun et al., 2012; Chen et al., 2012a), an oxidized form of graphene. GO consists of various groups, such as hydroxyl, carboxyl, and epoxy groups, which are beneficial to enhance dispersibility and eliminate pollutants in water (Park and Ruoff, 2009; Yang et al., 2012a). Unlike the special oxidation processes of CNTs, the preparation of GO is significantly easier (Zhao et al., 2011b) using Hummers' method (Hummers and Offeman, 1958) and offers the potential of cost-effective and large-scale production (Sun et al., 2012; Yang et al., 2012a). Differing from the concern of CNTs to human health (Simate et al., 2012), GO reveals better biocompatibility (Chen et al., 2012a, 2012b). In summary, all aforementioned advantages, including large surface area, large amount of activated functional groups, good dispersibility in water, relatively easy preparation method and biocompatibility, demonstrate the possibility of applying GO as an excellent water treatment agent.

In fact, previous studies (Ramesha et al., 2011; Sun et al., 2012; Yang et al., 2012a; Zhao et al., 2011b; Zhu et al., 2012) have already proven that GO is an efficient absorbent to remove metal ions and various kinds of organic matters such as cationic dyes, anionic dyes, and ionizable aromatic compounds from water. However, no published work has addressed the topic of using GO as a flocculant thus far. When processing extremely thin thickness in the Z-axis, GO has a large size in the XY plane, reaching several micrometers (Zhu et al., 2012). Thus, the net-like structure is expected to have great potential for providing the improved ability of sweeping flocculation for contaminants in water.

Aside from contaminant removal efficiency, the floc properties are also of great importance (Yang et al., 2012c). Generally, denser and larger flocs are preferred to reduce the cost in water treatment (Moghaddam et al., 2010; Yang et al., 2012c). Porous and irregular flocs have been found geometrically fractal, thus fractal theory can be used as a useful approach to evaluate the floc properties. In previous studies (Chakraborti et al., 2000; Yang et al., 2012c), image analysis (IA) has been successfully applied to describe the floc properties. In IA, larger two-dimensional fractal dimension (D_2, defined by the power law relationship between projected area A and characteristic length l) presents more compacted flocs, which is one of the important aspects in flocculation.

Besides, for guiding the application of flocculants in water purification more scientifically and effectively, systematical studies on the flocculation mechanism are very necessary. Different steps occur in the water purification process for various kinds of wastewater, which may result in different flocculation mechanisms (Gregory, 2006; Simate et al., 2012; Yang et al., 2012c). For particulate contaminants, the step where particles are destabilized and form small aggregates is also known as coagulation, whereas the step in which larger flocs are formed due to bridging is called flocculation. Despite the subtle difference, flocculation is often discussed in combination with coagulation synonymously (Simate et al., 2012). For soluble contaminants, the stages are more complicated. In addition to the coagulation and flocculation steps, there still exists an adsorption process, i.e. soluble matters are facile to adsorb onto the flocculants and form insoluble complexes. All these steps occur continuously or simultaneously (Yang et al., 2012c). Furthermore, binding forces between flocculants and contaminants also vary significantly in different flocculation systems. For example, previous studies on adsorption have found that GO can bind with some solutes through charge attraction, which is usually dominant when GO and contaminants have opposite charges (Ramesha et al., 2011), hydrogen-bonding (Chen et al., 2012a; Hartono et al., 2009), Lewis acid–base interaction (Goncalves et al., 2011; Hartono et al., 2009), $\pi-\pi$ stacking (Chen et al., 2012a; Hartono et al., 2009; Hyung et al., 2007; Yang et al., 2012a; Zhao et al., 2011a, 2011b) and so on.

In view of all the aforementioned aspects, this study aims to explore the possibility of using GO as a novel flocculant for the first time. For giving a more systematical investigation of the flocculation properties of GO, particulate contaminants (kaolin and hematite) and soluble ones (humic acid (HA) and cationic dye 7GL) with different surface charges were all selected. Therein, kaolin and HA are negatively charged, 7GL is positively charged, and hematite has an isoelectric point (IEP) of approximate 9.5. Since initial pH of water can change the properties of contaminants (Simate et al., 2012; Yang et al., 2011a, 2012c), each synthetic wastewater was tested under acidic, neutral and alkaline conditions, respectively. Floc properties were especially investigated in combination with fractal theory. In addition, the flocculation performance of raw graphite and polyaluminum chloride (PAC) has been also studied for further comparison, since graphite is the parent material of GO and PAC is one of the most traditional and popular inorganic flocculants. Furthermore, the flocculation mechanism of GO in treating different wastewater was also studied in detail from the floc properties and zeta potentials (ZPs) of the supernatants.

2. Materials and methods

2.1. Materials

Natural graphite flakes (purity: 99.85%; average particle diameter: 27.88 μm) were purchased from Sinopharm Chemical Reagent Co., Ltd. PAC ($[Al_2(OH)_nCl_{6-n}]_m$, $n = 3.6-5$, $m < 10$, Al_2O_3 content>28%) was purchased from Guangzhou Yurun Chemical Technology Co., Ltd. Kaolin (average particle diameter: 4.18 μm; Sinopharm Chemical Reagent Co., Ltd.), HA (fulvic acid type; 90% purity, Aladdin Chemistry Co., Ltd.), hematite (average particle diameter: 0.18 μm; Strem Chemicals Inc.), and cationic light yellow dye (7GL) (Rugao Xingwu Chemical Co., Ltd.) were used without further purification. The particle size distribution curves of graphite, kaolin and hematite are shown in the Supporting information Fig. S1. All other chemicals were purchased from Nanjing Chemical Reagent Co., Ltd. Distilled water was used in all experiments. GO was prepared through the modified Hummers' method (Hummers and Offeman, 1958). The detailed preparation route and characterization methods of GO are described in the Supporting information Texts 1 and 2.