Science of the Total Environment 532 (2015) 556–563

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Formation of complexes between hematite nanoparticles and a non-conventional galactomannan gum. Toward a better understanding on interaction processes

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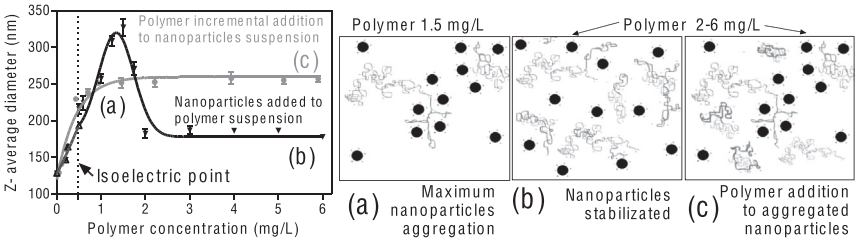
HIGHLIGHTS

- *Vinal* gum has a polydispersity index of 0.65 and a Z-average diameter of 300–450 nm.
- *Vinal* gum and hematite particles have opposite zeta potential values at pH 5.5.
- 0.2–2 mg/L concentration of *vinal* gum promoted aggregation of hematite nanoparticles.
- Different interactions are involved: electrostatic, steric and polymer bridging.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 April 2015
Received in revised form 30 May 2015
Accepted 30 May 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Hematite nanoparticles
Vinal gum
Polymer–nanoparticle interaction
Aggregation kinetics
Iron oxides

ABSTRACT

The physicochemical characteristics of hematite nanoparticles related to their size, surface area and reactivity make them useful for many applications, as well as suitable models to study aggregation kinetics. For several applications (such as remediation of contaminated groundwater) it is crucial to maintain the stability of hematite nanoparticle suspensions in order to assure their arrival to the target place. The use of biopolymers has been proposed as a suitable environmentally friendly option to avoid nanoparticle aggregation and assure their stability. The aim of the present work was to investigate the formation of complexes between hematite nanoparticles and a non-conventional galactomannan (*vinal* gum — VG) obtained from *Prosopis ruscifolia* in order to promote hematite nanoparticle coating with a green biopolymer. Zeta potential and size of hematite nanoparticles, VG dispersions and the stability of their mixtures were investigated, as well as the influence of the biopolymer concentration and preparation method. DLS and nanoparticle tracking analysis techniques were used for determining the size and the zeta-potential of the suspensions. VG showed a polydispersed size distribution (300–475 nm Z-average diameter, 0.65 Pdi) and a negative zeta potential (between −1 and −12 mV for pH 2 and 12, respectively). The aggregation of hematite nanoparticles (3.3 mg/L) was induced by the addition of VG at lower concentrations than 2 mg/L (pH 5.5). On the other hand, hematite nanoparticles were stabilized at concentrations of VG higher than 2 mg/L. Several phenomena between hematite nanoparticles and VG were involved: steric effects, electrostatic interactions, charge neutralization, charge inversion and polymer bridging. The process of complexation between hematite nanoparticles and the biopolymer was strongly influenced by the preparation protocols. It was concluded that the aggregation, dispersion, and stability of hematite nanoparticles

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http://dx.doi.org/10.1016/j.scitotenv.2015.05.134

depended on biopolymer concentration and also on the way of preparation and initial physicochemical properties of the aqueous system.

1. Introduction

Iron oxide nanoparticles promote rapid degradation of contaminants, reduction of the degradation time by favoring the delivery of suspensions (Comba and Sethi, 2009) and reductive precipitation of metal ions (Li and Zhang, 2007). These properties, which are related to their size, high surface area, the possibility of surface modifications and high reactivity, make them suitable for many applications (Comba and Sethi, 2009; McHenry and Laughlin, 2000). Hematite (α-Fe_2O_3) is one of the several iron oxide polymorphs, like magnetite and maghemite (Xu et al., 2012). Magnetic particles with biocompatible coating have been used for biomedical applications such as in vitro diagnosis, magnetic resonance imaging studies and treatment of some malignant cells, since excess iron could be processed by the body (Berry, 2006). The application of iron oxide particles can be regarded as an innovative technology for the remediation of groundwater contaminated by heavy metal ions and recalcitrant contaminants (Xu et al., 2012; Zhang, 2003). The stability of iron oxide suspensions is crucial in order to assure the arrival to the desired target place and the efficiency of remediation (Dickson et al., 2012).

Hematite nanoparticles (hematite NPs) were found to inverse their surface charge and to enhance their stability by the addition of polysaccharides like guar gum (Tiraferri et al., 2008; Tiraferri and Sethi, 2009), alginate (Chen et al., 2006), Arabic gum (Williams et al., 2006), and carboxymethyl cellulose (He and Shao, 2007). The interaction of hematite NPs with natural organic matter (NOM) has been studied before to investigate the environmental impact of hematite nanoparticles when entering natural aquatic systems (Baalousha, 2009; Nidhin et al., 2012; Palomino and Stoll, 2013). The adsorption of negatively charged humic substances on the positively charged surface of hematite NPs was found to strongly modify their surface charge by inducing charge inversion and thus enhanced their stability through electrostatic repulsion and steric effects. Illés and Tombácz (2006) have found that for a certain natural organic matter concentration the aggregation of iron oxide particles was induced, but at higher NOM concentration the Fe_2O_3 NPs were stabilized. Ferretti et al. (2003) also found that at a given schizophyllan/hematite ratio the flocculation rate was maximum, but the hematite particles were stabilized at higher concentration of polysaccharide. Among the used additives, biopolymers are generally preferred as they are environmentally safe (Nidhin et al., 2012), biodegradable, biocompatible and harmless toward organisms (Comba and Sethi, 2009). In the presence of biopolymers, the inorganic particles (i.e. zero valent iron, hematite or magnetite) have shown to modify their stability and thus their transport properties (Comba and Sethi, 2009; Chen et al., 2006; Nidhin et al., 2012; Tiraferri and Sethi, 2009; Williams et al., 2006; Gómez-Lopera et al., 2001). Many types of interactions have been reported between organic material and inorganic colloids: hydrophobic, electrostatic, van der Waals, ligand exchange, chelation, cation bridging and H-bonding (Philippe and Schaumann, 2014). In some cases, a non-electrostatic stabilization is needed to keep the NP reactivity toward contaminants unaffected for a particular application in targeted systems (Tiraferri et al., 2008; Williams et al., 2006). Galactomannans like guar gum or locust bean gum form solutions which are relatively insensitive to pH changes, addition of electrolytes and heat treatments (Mathur, 2012; Sittikijyothin et al., 2005). The use of green biopolymer as hematite NP coating agent is of great interest. In this sense, the use of the pH-stable galactomannans (Mathur, 2012) extracted from highly available sources offers the possibility to control NP stabilization in a simple way and with less environmental impact. Thus it is necessary to explore innovative and suitable resources for their extraction. A promising biopolymer source is a leguminous plant known as *vinal* (*Prosopis ruscifolia*), from the mesquite family native of North-East Argentina, very abundant in that region, being still an unexploited resource. A galactomannan gum (a sugar polymer of mannose branched with galactose called *vinal* gum (VG)) extracted from *vinal* seeds has similar structure and physicochemical properties as guar gum (Busch et al., 2015). Expanding *vinal* uses will highly impact the local development of innovative materials extracted from natural resources. Considering that the nature and source of the organic material can affect its role while interacting with inorganic colloids, and produce changes in aggregation and sedimentation behaviors (Wilkinson et al., 1997), it is important to study original, innovative biopolymer–inorganic particle interactions and the corresponding complexation processes. The purpose of the present work was to investigate the complex formation and interactions between hematite NPs and a galactomannan gum obtained from *vinal* (*P. ruscifolia*). The resulting changes of the hematite NP surface charges and Z-average diameters as a function of a green biopolymer concentration, dispersion stability and aggregation conditions were considered.

2. Materials and methods

2.1. Materials

Sodium hydroxide (Titrisol 1 M®, Merck & Co. Inc., NJ, USA), ethanol absolute (Biopack, Sistemas Analíticos S.A., Zárate, Argentina), HCl (analytical grade — Sigma Aldrich Co., St. Louis, MO, USA) were used. All water solutions were prepared with MilliQ water with a minimum resistivity of 18 $M\cdot\Omega\cdot cm^{-1}$.

2.2. Hematite synthesis

5.408 g of $FeCl_3\cdot 6\ H_2O$ were added to 2 L of 0.02 M HCl solution at 98 °C. The solution was kept at 98 °C for 10 days (He et al., 2008; Schwertmann and Cornell, 1991). Then, it was cooled to 25 °C and dialyzed with SpectrumLabs Spectra/Por 12–14 kDa dialysis membrane in order to remove the ions. A final hematite NP suspension of 1.64 ± 0.04 g/L was obtained by using the molar extinction coefficient equal to $4.06 * 10^3\ M^{-1}\cdot cm^{-1}$ at 385 nm (Schwertmann and Cornell, 1991) within a HACH Lange DR-3800 spectrophotometer (HACH Lange, Derio Vizcaya, Spain). The NPs were stored as a 0.2 g/L suspension in a cold and dark environment. After image analysis of more than 50 SEM pictures by Palomino and Stoll (2013), the mean SEM diameter of the individual nanoparticles was found equal to 53 ± 5 nm confirming that the nanoparticle sizes were reasonably monodispersed. The Z-average hydrodynamic diameter was found equal to 94 ± 3 nm at pH = 3, indicating the presence of dimmers and trimers in solution.

2.3. Separation of seeds and extraction of vinal gum

Vinal (*P. ruscifolia*) seeds were separated by milling the pods (from Formosa province, Argentina, in 2010) and passing the obtained product through sieves (Sonytest, Rey & Ronzoni S.R.L., Buenos Aires, Argentina). Then, the endosperm (20 g seeds) was manually separated after alkaline treatment (Chaires-Martínez et al., 2008) and stirred in 100 mL of double distilled water for 24 h. After 3 min at 4500 rpm centrifugation, the supernatant was poured into 200 mL of absolute ethanol and the biopolymer flocculated during the storage in the refrigerator (8 °C) for 3 h. VG was then manually separated, dry in oven at 25 °C (300 mbar) for 24 h, and further purified by solubilizing in 50 mL of double distilled water and