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A novel approach for synthesis of exfoliated biopolymeric-LDH hybrid nanocomposites via in-stiu coprecipitation with gum Arabic: Application towards REEs recovery

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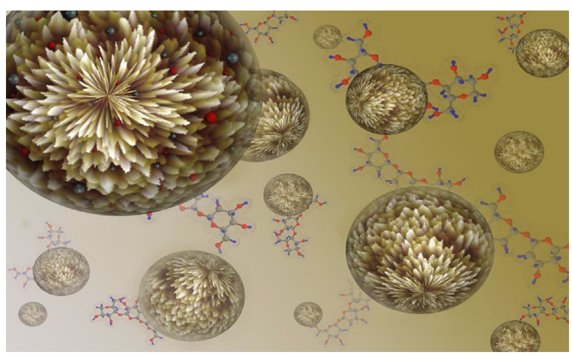
HIGHLIGHTS

- LDH-exfoliation was possibly by in-situ coprecipitaion in biopolymeric matrix.
- The divalent ions of LDH affects the morphology and characteristics of GAnXA.
- The GA5MA showed superior adsorption and reusability for REEs compared to others.
- All GAnXA were highly selective for Sc and HREEs removal favorable over LREEs.

GRAPHICAL ABSTRACT



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ABSTRACT

Delamination and exfoliation of layered double hydroxides (LDH) is an interesting way for the synthesis of novel nanocomposites. Herein, we report the synthesis of various exfoliated biopolymeric-LDH nanocomposites via in-situ coprecipitation method with gum Arabic (GA). The influence of various divalent ions on the morphological characteristics of GAnXA (n = wt% of GA and X = Mg, Ca, Ba, Sr) was explored Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and Scanning Electron Microscopy (SEM). X-ray diffraction pattern was used for the determination of phase composition of synthesized nanocomposites. The surface functional groups of GAnXA were investigated by Fourier Transform Spectroscopy (FTIR). Furthermore, the surface charge characteristics was explored by zeta potential analysis. Specific surface area of GAnXA was determined by BET analysis. The overall adsorption of REEs decreased with an increase in ionic size of divalent ions and the noticeable difference in the morphologies of exfoliated GAnXA was observed. In a single component system, the REEs adsorption capacities followed the order: Sc > Y > Nd > Ce > Eu > La, whereas, in multicomponent system, adsorption seems to be competitive and presence of competing ions affect the overall REEs removal. Moreover, HREEs removal superseded over LREEs and the nanocomposites (GA5CA, GA5SA, GA5BA) were highly selective for Sc recovery. The post-adsorption FTIR and SEM results revealed the importance of surface hydroxyl and carboxyl functional groups enacting as the principal REE binding sites. Overall,

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ability to extract REEs at pH 4 (slightly acidic) presented a facile route for the recovery and separation of REEs from aqueous medium and enhances the possibility of its use in many industrial applications.

1. Introduction

REEs consists of group of 17 elements with 15 lanthanides and two pseudo lanthanides (Sc,Y) with same electron configuration. These are then further categorized as LREEs (light rare earth elements: La-Eu) and HREEs (heavy rare earth elements: Gd-Lu) based on their atomic numbers, where Sc is categorized as LREEs and Y as HREEs [1–5]. The application of REEs in various modern applications resulted in escalation in their demand [6,7]. On the other hand, the gap between the world's demand and supply is increasing [6] which serves as a motivation for the search of new methods to recover REEs from secondary sources for instance industrial residues [1]. Several existent methods for the recovery of REEs are: ion exchange, membrane separation, chemical precipitation, solvent extraction, adsorption, etc. [8–13]. Compared to the conventional methods, adsorption was found as one of the most cost efficient, eco-friendly and economical method for the recovery of REEs.

Gum Arabic (GA) also known as Gum Acacia, a natural biopolymer, exudated from the trunks and barks of Acacia tree and consists of amino acids linked to short arabinose side chain [14,15]. GA is found to be a suitable biomaterial for several technological applications due to its biological, chemical and physical properties. GA has already been employed for the synthesis of various new hybrid materials of technological interest due to its non-toxic nature, high solubility, low viscosity and good emulsifying characteristics [14,16]. Several studies reported GA based nanocomposites viz. GA-Fe_3O_4 [14], GA loaded MgO nanoflower [17], GA-AgNPs [15], GA-g-PAM/SiO_2 [5] etc. The novel production of hybrid organic-inorganic materials synthesized at nanoscale interface displays new properties based on the synergic effect of both organic and inorganic part. For the preparation of such hybrids layered double hydroxides (LDH) have been considered as a favorable host.

LDH often termed as anionic clays are compounds composed of positively charge brucite like layers [18]. LDH (bi-dimensional solids) mainly consists of divalent and trivalent cations and various inorganic or organic anions are introduced between the layers to compensate the positive charge [4]. LDH has been widely used as adsorbents [4,19,20], catalysts [21], cement additives [22] and as drug delivery host [23]. Delamination and exfoliation of LDH is an interesting way for the synthesis of novel inorganic-inorganic or organic-inorganic nanocomposites [24]. Nevertheless, the exfoliated LDH are of more interest compared to intercalated nanocomposites due to better dispersion in polymer matrix [25], whereas, exfoliation of LDH is quite difficult compared to cationic clays like montmorillonite [26]. The possible ways to synthesize the exfoliated polymeric-LDH nanocomposites are: (a) intercalation of the monomer molecules and in situ polymerization, (b) direct intercalation of extended polymer chains, (c) pre-exfoliation and followed by mixing with polymer. Researchers in past used the above mentioned methods for preparing exfoliated polymer/LDH nanocomposite by using variety of polymers such as polyacrylate [27], polyimide [28], polymethyl-methacrylate [29], polycaprolactone [30], polystyrene [31], polyvinyl alcohol [32], etc. The intercalation of various biopolymers in LDH has been reported [4] by either reconstitution, anion exchange or coprecipitation method [33], however, no evidence in literature was found towards the synthesis and application of exfoliated biopolymer-LDH nanocomposites.

Therefore, this work provides a novel and efficient strategy for synthesis of exfoliated biopolymeric-LDH (GAnXA) by in-situ coprecipitation method. The change in shape, size and morphology of exfoliated GAnXA was investigated by exchanging divalent cations (Mg, Ca, Sr, Ba) of LDH matrix and wt% of GA. The application of exfoliated GAnXA nanocomposites towards recovery of REEs was investigated in detail. Moreover, the studies had been carried out in single and multicomponent system, with or without competing ions and for the REEs trend on GAnXA nanocomposites.

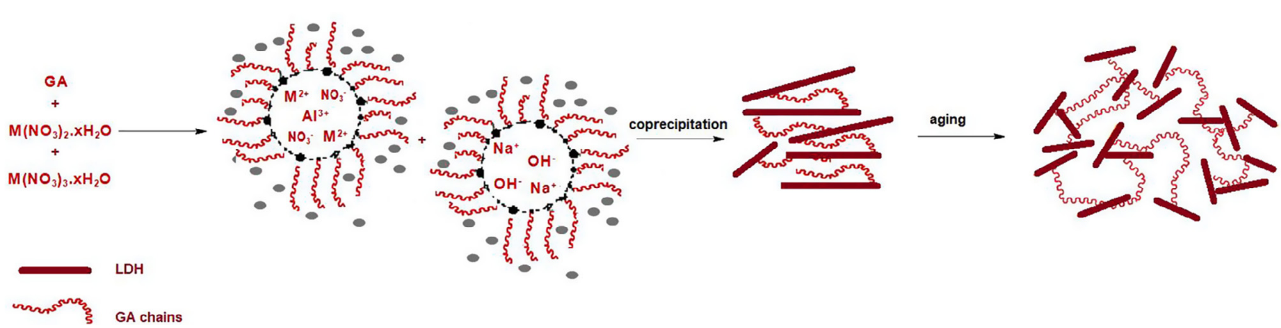
2. Materials and methods

2.1. Chemicals

Gum Arabic (GA) from acacia tree, sodium hydroxide (NaOH), hydrochloric acid (HCl), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) were obtained from Sigma Aldrich. Barium nitrate ($Ba(NO_3)_2$), and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were supplied by Acros Organics and strontium nitrate ($Sr(NO_3)_2$) was procured from Alfa Aesar. pH adjustment was done using 0.1 M NaOH/HCl solution. All the chemicals are of reagent grade and used without further purification.

2.2. Synthesis of GAnXA

The exfoliated GA-LDH was prepared by in-situ coprecipitation method (Scheme 1). Briefly, 2 g of GA (2 wt%) was dissolved in 100 mL of distilled water with constant stirring (300 rpm) at 70 °C for 1 h. Thereafter, 0.75 M $Mg(NO_3)_2{\cdot}6H_2O$ and 0.25 M $Al(NO_3)_3{\cdot}9H_2O$ (Mg:Al = 3:1) was added in GA solution and stirred for 2 h. The pH of solution was adjusted to 10 by slow addition of NaOH. The resulting GA-LDH precipitates were aged for 18 h, separated by centrifugation (EPPENDORF 5810) and washed with water several times. Then, the final product obtained was freeze dried (CHRIST Alpha 2-4 LD-Plus) and ground to get fine powder by IKA Tube mill control. The GA-LDH nanocomposites with $Ca(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$ were also prepared using the same method. Moreover, same synthesis conditions were employed for each composition of the materials containing 5 wt%



Scheme 1. Schematic illustration of GAnXA via in-situ coprecipitation method.