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Nanocrystalline magnesium oxide from dolomite *via* poly(acrylate) stabilized magnesium hydroxide colloids

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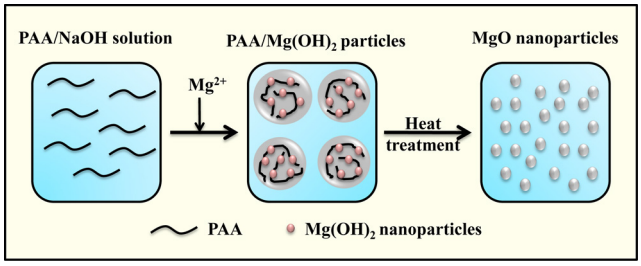
HIGHLIGHTS

- Poly(acrylate)-encapsulated magnesium hydroxide colloid is prepared.
- Dolomite is used as the magnesium source in preparing MgO nanoparticles.
- The poly(acrylate)-$Mg(OH)_2$ composite is heated to synthesize MgO nanoparticles.
- Thermal stability of poly(acrylate) is greatly enhanced by magnesium hydroxide.
- MgO nanoparticles adsorb methylene blue.

GRAPHICAL ABSTRACT



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ABSTRACT

MgO nanoparticles are in high demand, valuable products with specific applications such as a bactericide, catalyst, ceramic material and as an adsorbent. Synthesis of MgO nanoparticles from naturally occurring dolomite is very important for the reduction of their production costs and for the value addition to naturally occurring, impure minerals such as dolomite. Therefore, in this paper, we report on an effective method to synthesize MgO nanoparticles using a novel colloid of poly(acrylate) (PA^-)-encapsulated $Mg(OH)_2$ composite, which has been prepared starting from dolomite. The composite is synthesized by adding $MgCl_2$, which was produced using dolomite, to a mixture of poly(acylic acid) (PAA) and NaOH. The composite is heated at 500 °C to produce MgO nanoparticles. The $Mg(OH)_2$ mineralized in the composite colloid is brucite nanoparticles with average crystallite size of 5 nm. The final product of MgO nanoparticles occurs in the crystalline form of periclase with average crystallite size of 20 nm. Incorporated $Mg(OH)_2$ nanoparticles enhance the thermal stability of PA^- by 160–200 °C. The sedimentation of the $Mg(OH)_2$ colloidal particles, which are stabilized by PA^-, is initiated after 18 h but it takes 2 weeks for complete sedimentation. On the other hand, the $Mg(OH)_2$ prepared in the absence of PAA/NaOH is completely sedimented after 18 h. A portion of 0.100 g of synthesized MgO nanoparticles can adsorb over 93% of methylene blue molecules from 5 ppm methylene blue aqueous solution at the equilibration of

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the adsorption, whereas the adsoption of methylene blue by the same amount of 300 μm sized MgO particles is very much lower; 35% being the best value when 0.100 g is used. The proposed method is of great industrial value due to the potential applications of byproducts in addition to MgO nanoparticles themselves.

1. Introduction

Synthesis of stable colloids of inorganic/organic hybrid materials is of growing interest in the design of novel materials [1,2]. Magnesium hydroxide [$Mg(OH)_2$] is such an inorganic material that can be encapsulated and stabilized by organic polymers for the development of advanced colloids and powders of hybrid materials with a wide range of applications [1,3–8]. Polymer additives are capable of restricting inorganic materials to nanoscale size and to stable the colloids by preventing aggregation during their preparation [9]. This is done by preventing the encounter of nanoparticles leading to their flocculation and subsequent sedimentation. The Polymer molecules, particularly those containing polar moieties such as —COOH, COO^-, C═O, —SH *etc.*, can interact with these inorganic colloidal particles through covalent bonding or through electrostatic interactions with the cationic sites of the inorganic particles. Polymers containing cationic groups, such as NH_3^+, can also interact with the anionic sites of the inorganic nanoparticles [1,3,7]. It is these interactions that encapsulate the inorganic nanoparticles within the polymer matrix, leading to the termination of their growth and thereby restricting the size of the nanoparticles [10]. Also, the polymer segments adsorbed onto the surface of the inorganic nanoparticles prevent the encounter of nanoparticles through polymer or steric stabilization of the colloidal nanoparticles [1,3,10]. These polymer-based colloids of composite materials can, therefore, be used to produce fresh nanoparticles of inorganic materials with specific sizes and morphologies [11]. Although the preparation of polymer-encapsulated colloids of $Mg(OH)_2$ nanocomposites is a timely needed requirement, there are only a limited number of reported studies on this process [5,7]. Moreover, poly(acrylic acid) (PAA) and its salts are widely used to synthesize inorganic/organic hybrid materials [12–15]. Nevertheless, to the best of our knowledge, PA^- has been employed only limitedly to synthesize $Mg(OH)_2$ colloids [3]. Usually, $Mg(OH)_2$ and their polymer-based composites are heat-treated to synthesize magnesium oxide (MgO) nanoparticles [16–19]. MgO is a valuable product with outstanding applications such as a bactericide, catalyst, ceramic material, material for toxic waste remediation and an adsorbent of toxic chemicals and dyes from effluents [17,20–25].

Most researchers have used commercially available Mg^{2+} salts to synthesize $Mg(OH)_2$ and MgO nanoparticles [16,19,26–28]. However, some naturally occurring minerals such as dolomite and magnesite can also be used as a source of Mg^{2+} which has the advantage of the low-cost raw materials and hence better suitability for industrial use when compared to commercial chemicals [29]. Dolomites are mineral constituents found in the sedimentary carbonate rocks as well as in crystalline limestones which are widely distributed throughout the world [30,31]. In the conventional method to synthesize $Mg(OH)_2$ and MgO using dolomite, calcined dolomite (CaO·MgO) is treated with brine to produce $Mg(OH)_2$ [32–35]. The synthesized $Mg(OH)_2$ is then heated to produce MgO. However, this method consists of several disadvantages, such as, complicated procedures cost of chemicals used to remove impurities in brine [32–35]. Furthermore, the final product may contain more impurities and, therefore, the product is less valuable since the purity is one of the key factors in the value estimation of the product. Hence, more an effective method is required to synthesize $Mg(OH)_2$ and MgO using naturally occurring minerals.

Herein, we report an economical and practical method to synthesize MgO nanoparticles with high purity, through novel stable colloid of PA^- encapsulated $Mg(OH)_2$ composite material which is prepared using calcined dolomite. We have communicated the preliminary investigations of the method in brief as an extended abstract elsewhere [36]. However, a comprehensive study on colloidal $PA^-/Mg(OH)_2$, had not been reported earlier, and is reported in this paper. Herein, the colloidal stability of the composite and its application to synthesize nanocrystalline MgO is described. Furthermore, the adsorption of methylene blue (MB) by the synthesized MgO nanoparticles is investigated. Since pure MgO nanoparticles are relatively expensive, the proposed method is very important with respect to value addition to natural mineral resources such as dolomite. Furthermore, the overall process is very important because of the applications of the byproducts other than $Mg(OH)_2$ colloids and MgO nanoparticles.

2. Experimental

2.1. Materials

Acrylic acid (AA) (99% purity), sodium peroxydisulfate (persulfate) (99.9% purity), hydrochloric acid (36.5% assay), sodium hydroxide (99.8% purity) and magnesium oxide (98% purity and particle size is about 300 μm) were purchased from Sigma–Aldrich. Dolomite samples were collected from the working marble quarries located in the central part (near the city of Kandy) of Sri Lanka.

2.2. Separation of calcium and magnesium components from dolomite

The dolomite samples were crushed, ground and the less than 100 μm sieved fraction was used. The powder obtained was heated at 1000 °C for 4 h in a muffle furnace to produce calcined dolomite (CaO·MgO). 5.00 g of calcined dolomite was added to 100.0 mL of a 0.50 M sucrose solution and stirred for an hour. The supernatant was filtered under suction to separate the precipitated MgO with impurities from the soluble calcium sucrate. The precipitate was added to 50.0 mL of a 1.0 M HCl solution and well stirred to separate $MgCl_2$ solution from acid insoluble impurities such as silicate minerals that are very often found in natural dolomitic rocks. The $MgCl_2$ solution thus obtained was separated by filtration under suction to yield a solution at a pH of 6.0. The procedure is illustrated in the flow chart given in Fig. 1.

2.3. Synthesis of $PA^-/Mg(OH)_2$

We have documented the preparation method, in brief, as an extended abstract elsewhere [36]. In brief, a stock solution of PAA was prepared (0.50 M of repeating unit) by radical polymerization of AA using 1.00 g of $Na_2S_2O_8$ initiator. 50.0 mL of PAA solution was mixed with 100.0 mL of 1.0 M NaOH solution and stirred for 30 min, maintaining over and above the amount of OH^- ions to completely convert all PAA to PA^- and Mg^{2+} to $Mg(OH)_2$. 25.0 mL of $MgCl_2$ produced using calcined dolomite was added dropwise to the PAA/NaOH mixture while stirring to prepare colloidal $PA^-/Mg(OH)_2$. The colloid was centrifuged at 5000 rpm for 15 min to obtain a sedimented product. The sediment was