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Intensification of ultrasound-assisted process for the preparation of spindle-shape sodium zinc molybdate nanoparticles

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ABSTRACT

In the present work, sodium zinc molybdate (SZM) nanoparticles were prepared using conventional and an innovative ultrasound assisted co-precipitation of sodium molybdate, zinc oxide and HNO_3 at different temperatures. Prepared product was characterized by XRD, TEM, FT-IR, particle size distribution (PSD), TGA and DTA techniques. TEM analysis shows the spindle-shaped morphology of the formed SZM nanoparticles. The average particle size of SZM nanoparticles is found to be lower in case of sonochemical method (78.3 nm) compared to conventional method (340.2 nm) which is attributed to faster solute transfer rate due to ultrasonic irradiation leading to rapid nucleation and restricted growth of SZM nanoparticles. Further, the kinetics of synthesis of SZM nanoparticles are studied using the sonochemical method at different operating temperature and conventional method at 80 °C. It is shown that the rate of reaction is significantly faster at 40 °C compared to other temperatures and also conventional method. This can be attributed to intense cavity collapse at lower temperature (low vapour pressure) compared to higher temperature (high vapour pressure) of the reaction mixture.

1. Introduction

Sodium zinc molybdate (SZM) has been identified as a novel corrosion inhibiting pigment and is recommended as non-toxic anticorrosive pigment for marine coatings as these pigments possess low toxicity as compared to chromate/lead based anticorrosion pigments [1]. SZM is essentially white and non-toxic pigment, which has anticorrosive properties better than those of zinc yellow and other commercially available pigments. Zinc yellow pigment has disadvantages such as its yellowish colour and toxicity. Corrosion protection of metals and the replacement of toxic compounds in paint formulations are the most important considerations claimed in the field of paint technology. Consequently, many attempts have been made to replace toxic pigments with those which do not have these disadvantages [2–4]. Many compounds have been proposed as possible replacements for chromates and lead compounds, but zinc phosphate and related substances have become the leading substitutes for toxic inhibitors [5–9]. Sodium zinc molybdate pigment can be applied as an anticorrosive pigment due to the following reasons (i) zinc element gives the anticorrosion performance by sacrificial mechanism, (ii) molybdate group partially dissolves in water and forms adsorbed inhibitive layer of metal complex on the metal surface, and (iii) it is white and nontoxic pigment. Sodium zinc molybdate acts as a corrosion inhibitor and hence used in many industrial corrosion protective coatings.

Recently, the study of physical and chemical effect of ultrasound irradiation on the synthesis of inorganic materials is rapidly developing into a major research area [10–14]. The chemical and physical effects arise from extreme adiabatic conditions (high temperature and pressure pulse) generated locally due to cavity collapse [15–18] and it is gradually becoming an important tool for the synthesis and modification of nanosized functional inorganic materials [19]. Further, the extreme conditions of high temperature, pressure and intense micromixing achieved during acoustic cavitation lead to the formation of nanometer sized particles with improved solute transfer and nucleation rate in aqueous suspension [19]. Hence the use of ultrasonic irradiation to prepare anticorrosive nanopigments is likely to improve the product distribution (lesser size) leading to well-dispersed nanoparticles to be used in the coatings with lesser dosage of nanopigments, which would reduce the overall cost [20–24].

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The present work focuses on the use of ultrasonic irradiation for the synthesis of nanometer sized anticorrosive SZM pigment. Further, a comparative study of the processes i.e. the conventional and sonochemical method used for synthesis of SZM nanoparticles is presented. Also, the kinetic behaviour during the synthesis of sodium zinc molybdate nanoparticles using the sonochemical method at different temperature and conventional method at 80 °C is reported. The effect of ultrasonic irradiation and temperature on particle size distribution of the sodium zinc molybdate is also discussed.

2. Theoretical aspects

It is well known that the presence of ultrasonic irradiation in the aqueous medium leads to a dissociation of water molecules in the cavitation bubble during transient collapse generating $H^{\cdot}$ and $OH^{\cdot}$ radicals. The radicals so formed may undergo recombination, generating if not utilized quickly, into H_2 and H_2O_2.

$$H_2O \xrightarrow{\text{Ultrasonic irradiations}} OH^{\cdot} + H^{\cdot} \quad \text{(i)}$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \quad \text{(ii)}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad \text{(iii)}$$

The synthesis of sodium zinc molybdate in the presence of ultrasonic irradiations may take place as per the following possible reaction mechanism.

$$2Na_2MoO_4 + ZnO + OH^{\cdot} + H^{\cdot} \xrightarrow{\text{Ultrasoni irradiations}} Na_2Zn(MoO_4)_2 + 2NaOH \quad \text{(iv)}$$

Sodium molybdate in the presence of ultrasonic irradiation can get drifted at very high velocity in the shock waves generated by the bubbles and undergo highly energetic intercollisions with ZnO. These collisions can leads to the formation of sodium zinc molybdate.Further, the chemical reaction of the formation of sodium zinc molybdate compound can be represented by the following reactions

$$2Na_2MoO_4 \rightarrow 4Na^{+} + 2MoO_4^{2-} \quad \text{(v)}$$

$$ZnO \rightarrow Zn^{2+} + O^{2-} \quad \text{(vi)}$$

$$HNO_3 \rightarrow H^{+} + NO_3^{-} \quad \text{(vii)}$$

$$4Na^{+} + 2MoO_4^{2-} + Zn^{2+} + O^{2-} + H^{+} + NO_3^{-} \rightarrow Na_2Zn(MoO_4)_2 + NaOH + NaNO_3 \quad \text{(viii)}$$

The overall reaction of the process is as follows:

$$2Na_2MoO_4 + ZnO + HNO_3 \rightarrow Na_2Zn(MoO_4)_2 + NaOH + NaNO_3 \quad \text{(ix)}$$

The reaction mechanism for the formation of sodium zinc molybdate is reported above. Out of these reactions Eqs. (i)–(iv) reports the reaction taking place in the ultrasound assisted environment. In these reactions, during the formation of sodium zinc molybdate $H^{\cdot}$ and $OH^{\cdot}$ radicals may be used. According to these reactions $H^{\cdot}$ and $OH^{\cdot}$ radicals are generated due to the collapse of cavitation bubble. The reaction (ii) and (iii) reports the recombination of radicals so formed to form H_2 and H_2O_2. Further, in reaction (iv) the formed $H^{\cdot}$ and $OH^{\cdot}$ radicals react with sodium molybdate and zinc oxide to get the required product [25–28]. Ultrasound plays an important role in producing physical and chemical effects in the reaction medium. The ultrasound wave passes through the medium in the form of alternate compression and rarefaction cycles, generating oscillatory motion of fluid elements, which creates intense turbulence and micro-mixing in the reaction medium. The physical and chemical effects generated by cavitation bubbles are well known [25–28]. The velocity of the bubble wall during compression or collapse phase may reach or exceed the sonic velocity in the liquid medium during high amplitude transient radial motion. At this instant of time, the pressure inside the bubble equals the external force of converging fluid elements during the compression phase and the gas–liquid bubble interface comes to an abrupt halt. Therefore, at this moment, the converging fluid elements in bubbles vicinity are bounced back and that generates a high pressure amplitude wave or a shock wave. This shock wave causes the drifting of solid particles in the medium at very high velocity and can undergo energetic inter-collisions leading to chemical reaction [25]. Further, the temperature and pressure inside this collapsing cavity reach intense conditions (~5000 K, ~500 bars) at the point of maximum compression during radial motion [25]. The expansion phase of the cavitation bubble is accompanied by large evaporation of solvent vapour in the expanding bubble and then during the compression phase some amount of vapour gets entrapped in the cavitating bubbles, which is subjected to intense conditions generated during bubble collapse. At these conditions, the vapour molecules undergo dissociation and generation of $H^{\cdot}$ and $OH^{\cdot}$ radicals and other molecular active species takes place. These radicals got diffuse out of the bubble due to the fragmentation of bubble at the time of maximum compression (implosion) and can induce chemical reactions. Based on this theory, we can propose the relation between physical and chemical effects of transient cavitation bubbles and the synthesis of sodium zinc molybdate. These are: (1) during ultrasonic irradiation $H^{\cdot}$ and $OH^{\cdot}$ radicals are formed due to an implosive collapse of cavitating bubble and these radical initiate the reaction between sodium molybdate and zinc oxide leading to the formation of sodium zinc molybdate. Further, some of the radicals recombine to form H_2 and H_2O_2 species. (2) This reaction may occur because of highly energetic intercollisions between the reactant species, which are directed at very high velocity due to the shock waves generated by the collapsing cavity.

3. Experimental

3.1. Materials

Zinc oxide (Analytical Grade, 99%), sodium molybdate dihydrate (Analytical Grade, 99%) and nitric acid (Laboratory Grade, 70%) were procured from S. D. Fine Chemicals Ltd, Mumbai and used without any further purification for the synthesis of SZM nanopigment. Deionized water (conductivity of <0.2 μS/cm) generated using the Elix 3 UV water purification system, has been used throughout the experimentation.

3.2. Synthesis of SZM nanoparticles by conventional method

The reactor used for the synthesis of SZM nanoparticles consists of glass vessel provided with constant rpm magnetic stirrer (Model RQ1210, Remi Metals Gujarat Limited, India, 400 rpm) by means of continuous heating. Initially, aqueous solution of sodium molybdate dihydrate and zinc oxide was prepared by adding 41.2 g sodium molybdate dihydrate and 16.3 g zinc oxide in 150 mL deionized water each. These prepared solutions were transferred to the reactor and subjected to constant magnetic stirring at 80 ± 2 °C. Also, an aqueous solution of nitric acid was prepared separately by the addition of 25 mL HNO_3 in 200 mL deionized water and was added continuously within 2 h 20 min at a rate of 1.6 mL/min to the reactor which contains the aqueous solutions of sodium