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Evaluation of new integrated photo-catalyst adsorbent for removal of haloacetonitriles from water

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Abstract

In this study, a new integrated photo-catalyst adsorbent is prepared to degrade the harmful organic compounds of water in the presence of light irradiation. A citric acid assisted sol-gel method was employed to perovskite $MoTiO_3$/GO nanocomposites preparation. The characteristics of the samples were performed by SEM, BET, FTIR and XRD analysis. Results showed that the synthesized $MoTiO_3$ nanoparticles with average size of 26 nm were successfully deposited onto the graphene oxide (GO) adsorbent. Increasing the content of GO up to 1.5 wt. % in nanocomposite has an increasing effect on specific surface area. MoTiO3/GO photocatalytic activity was investigated by the haloacetonitriles (HANs) decomposition under UV irradiation. The $MoTiO_3$/ (GO, 1.5wt. %) nanocomposite displayed significant HANs removal capability up to 98.24% and excellent photocatalytic activity after 120 minutes of UV irradiation. Therefore, it can be said that the $MoTiO_3$/GO is a potential photo-catalyst for effective wastewater treatment of disinfection by-products (DBPs) and future industrial applications.

Keywords: *Graphene oxide, Haloacetonitrile, MoTiO3 nanocomposite, Photo-catalyst adsorbent*

1. Introduction

A safe supply of drinking water is vital to our health and well-being. Untreated water sources can contain harmful microorganisms that can cause serious problems or, in some cases, death [1]. Chlorination of drinking water is a proven method with an excellent safety record [2]. Many people around the world receive quality-disinfected drinking water from public water supplies, but chemical disinfection has created health problems. Chlorine is present in disinfected water in the form of hypochlorite and hypochlorous acid, which reacts with organic substances such as humic acid and fulvic acid, and disinfection byproducts include haloacetic acid (HAAs), trihalomethane (THM), chlorophenols, and haloacetonitriles (HANs) creates [3]. HANs are nitrogenous disinfection by-products (DBPs) that formed by the reaction between chlorine, chloramine or bromine disinfectants and natural organic matter present in drinking water supplies [4]. There are many different types of methods such as membrane filtration [5], adsorption [6-8], ozonation [9], photo-catalyst [10], etc. have been used to eliminate the DBPs from water effectively.

Photo-catalysts have the ability to destroy organic and inorganic pollutants using visible light, so it has the best potential to replace conventional wastewater treatment technology. Various compounds have been used as photo-catalysts for photo-degradation of many pollutants from water [11]. However, using these materials has its own problems. The main drawback of photo-catalytic nanoparticles is that they agglomerate when used in slurry form, which greatly reduces photo-catalytic performance [12-14]. The polar and non-porous surface of the photo-catalyst also reduces adsorption of impurities to its surface, thereby reducing the rate of photo-degradation. The photo-catalyst immobilization on the adsorbents is one of method that used to treat these problems.

An integrated photo-catalyst adsorbent can be degraded the harmful organic compounds in the presence of UV/visible light irradiation [15]. This combination preserves the properties of both individual components and overcomes to the problems such as fast recombination of photo-generated electrons and low absorptivity [16]. There had been many support materials that exhibit high specific surface area and dispersing ability which enhance excellent performance. Graphene oxide (GO) is one of the materials that is widely used in wastewater treatment due to its unique properties such as large surface area, mechanical stability, tunable electrical and optical properties [17].

In this work, the novel perovskite $MoTiO_3$/GO nanocomposite has been prepared and introduced. The characterizations of $MoTiO_3$/GO nanocomposite were done by scanning electron microscopy (SEM), fourier transform infrared spectra (FTIR), Brunauer-Emmett-Teller (BET) and X-ray diffraction (XRD) analysis. Finally, adsorption and photocatalytic activity evaluation of nanocomposite were examined on haloacetonitriles.

2. Experimental

$(NH_4)_6Mo_7O_{24}•_4H_2O$, Ti $(NO_3)_4$ and citric acid were supplied from Sigma-Aldrich (USA). GO was purchased from Merck (Germany). A mixture of haloacetonitriles including chloroacetonitrile (C2H2ClN), dichloroacetonitrile (C2HCl2N), trichloroacetonitrile (C2Cl3N), bromo-acetonitrile (C2H2BrN), and dibromoacetonitrile (C2HBr2N) were supplied from Alfa Aesar (Ward 116 Hill, MA).

2.1 Graphene oxide pre-treatment

The following procedure was done to graphene oxide pretreatment:

At the beginning, 3 grams of graphene oxide were refluxed in 150 ml of 2 M potassium hydroxide solution containing 1% by weight of sodium dodecyl sulfate at 120°C for 2 hours. Then the resulting mixture was cooled at room temperature, washed with DI water and filtered through a filter membrane with a pore diameter of 0.2 µm. Next, the sample was refluxed in concentrated nitric acid (65wt. %) for 24 hours with continuous stirring. The final product was washed with DI water and dried at room temperature.

2.2 MoTiO3-GO nanocomposite preparation

Sol-gel citrate method was used to prepare MoTiO3/GO nanocomposite. At first, equimolar of titanium nitrate (Ti (NO3)4) and ammonium heptamolybdate tetra hydrate ((NH4)6Mo7O24•4H2O) precursors were mixed by DI water. Then sol-gel agent (citric acid) was added in to the above mixture and the pH was adjusted to 6 by (NH4)2CO3 (1M). After stirring and sonicating the solution for 10 minutes, 5 grams of GO (at different concentrations of 0.5, 1, 1.5 and 2wt.%) were added to the resulting mixture and the mixture suspension was stirred and the temperature was set to 60°C and evaporated to obtain the sol-gel. The resulting gel was formed by the decomposition of nitrate ions due to the release of NOx gas. Then it was dried in a vacuum oven at 100°C for 3 hours. Then, the precursor is calcined at 1000°C for 5 h with a heating rate of 5 °C/min, and the final product was marked as MoTiO3/GO.

2.3. Characterization

The morphology of samples was characterized using SEM (KYKY-EM3200) with an accelerating voltage of 26 kV. The structural study of the samples was evaluated by BET (Micrometrics, ASAP 2020 analyzer). XRD measurements of cast PEDOU membranes were conducted on a DJ-10 Mini Desktop X-ray with Cu Kα radiation (wavelength: 1.5 Å) at 45 kV and 20 mA. FTIR was done by a Nicolet Nexus 670 FTIR spectrophotometer to identify the functional groups of integrated photo-catalyst adsorbent.

2.4 Adsorption and photo-catalytic study

The degradation experiment of HANs was carried out in a Xenon Lamp Photo-chemical Reactor (BL-GHX-I model) equipped with a 500W medium pressure Xenon lamp as the illumination source (wave length λ> 400nm, irradiation intensity 122.5 mW/cm2). In a typical adsorption and photo-catalytic measurements, 2 mg of integrated photo-catalyst adsorbent material was added into 150 mL HANs solution and sonicated for 20 min. To achieve the enrichment of adsorption-desorption equilibrium among the $MoTiO_3$-GO and HANs solution, the mixture was stirred in a dark continuously at least in 60 min at ambient temperature and pressure. Then, a sample was taken from the supernatant solution and the equilibrium concentrations of HANs was determined by a gas chromatography–mass spectrometry (GC–MS) (GCMS-QP2010 SE, Shimadzu, Japan). The adsorption performance for HANs removal was calculated using Eq. (1) [18]:

$$\text{HANs Removal (\%)} = (C_0-C_f)/C_0 \times 100 \quad (1)$$

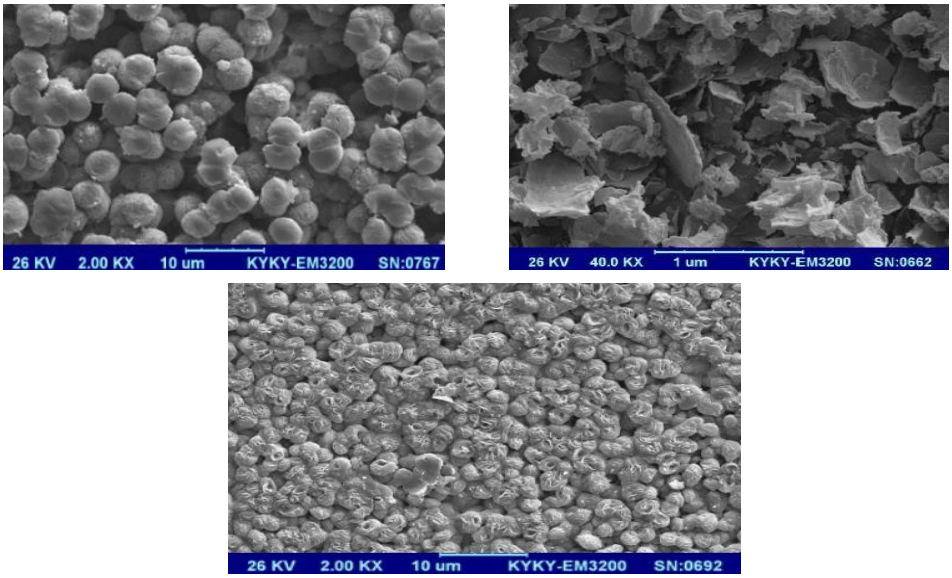

Fig. 1. SEM images of (a) $MoTiO_3$, (b) GO, and (c) $MoTiO_3$/ (GO 1.5 wt. %).