Ultrasonication synthesis of PVA/PVP/α-MnO$_2$-stearic acid blend nanocomposites for adsorbing Cd^{II} ion

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ABSTRACT

In this research, the functionalization of α-MnO$_2$ nanorods (NRs) was conducted with stearic acid (SA) through solvothermal technique. The α-MnO$_2$-SA NRs were used as nanofiller for the preparation of blend nanocomposites (NCs) based on poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) by ultrasonic irradiation. The results exhibit that with increasing in α-MnO$_2$-SA quantity, the thermal stability of blend NCs was improved. Morphological studies revealed that α-MnO$_2$-SA with rod structure and a diameter size of 25–80 nm was uniformly dispersed in the PVA and PVP matrices. The use of ultrasonic was responsible for these great homogeneities which could not be achieved by mechanical or magnetically stirring. The prepared blend NCs were exploited as an adsorbing for uptake of Cd^{II} ion from the aqueous system. The results indicated that they can be potentially utilized for the elimination of Cd^{II} ion from an aqueous system with q$_m$ of 47 (mg g^{-1}).

1. Introduction

Nowadays, contamination of water with heavy metals is of the serious environmental problems owing to their non-biodegradability, toxicity, and agglomeration in the body [1]. Among the known heavy metals, cadmium is toxic and carcinogenic even at little contents that cause adverse health effects in humans [2,3]. Thus various techniques have been expanded for uptake heavy metals from the infected waters. Among these techniques, adsorption is the most efficient technique because of its plainness, easiness of utilization and good performance in various concentrations [1]. Therefore, investigations have lately centralized on the application of new substances for adsorption of heavy metals from aqueous systems. Remarkable progresses have been achieved in technology by proposed properties of novel polymeric materials link such as blends, nanocomposites (NCs). Polymeric blends are provided using physical combining of double or several polymers and they improve properties of the polymeric materials [4]. Change the matrix from one pure to blend will make high differences in terms of physicochem properties and application and would bring new materials for use which each alone could not have it. Thus, this method is a useful technique for designing materials with a wide variety of properties. With the ever-growing of the environmental hazards, bio-chemicals such as PVA and PVP grab more attention in last decades [5,6]. PVA subtends polar hydroxyl groups connected to alternating carbon atoms

that make it excellent adsorbent for the adsorption of heavy metals [7,8]. The PVP lactam ring comprises a proton accepting carbonyl group, while PVA has hydroxyl groups and therefore, hydrogen bonds are expectable among them [9–11]. So, the introduction of the PVP in the PVA NC with good compatibility can improve the properties such as adsorption of heavy metals, physical and thermal properties due to the presence of strong hydrogen bonding interactions between PVP and PVA NC.

Usage of ultrasonic irradiation is a simple, green, and low-cost route for the preparation blend NCs. With the usage of ultrasonic, extraordinary reaction conditions like activation surface, high pressure, and high temperature are created for a very short time in a liquid that cannot be achieved by other methods such as mechanical or magnetic stirring. These reaction conditions are created by cavitation microbubbles (formation, growth, and collapse of microbubbles in a liquid). With collapsing of microbubbles, the concentrated energy stored in the microbubbles release within a very short time (with a heating and cooling rate of $> 10^{10}$ K s^{-1}) [12]. Furthermore, this route provides an excellent homogeneous blend NC with a good dispersion and distribution that is necessary to obtain a good blend NC with improved properties. Mallakpour and Jarahiyan reinforced the PVA/PVP blends using CuO nanoparticles through ultrasonic irradiation technique [13]. The results showed that thermal stability, morphology, and optical property were improved in comparison with the pure blend. In other work,

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Mondal et al. prepared blend NCs PVA/PVP/sodium montmorillonite by sonication and investigated the effect of PVP on the morphology and physical properties of PVA/sodium montmorillonite NC films [14].

One of the popular substances is manganese dioxide (MnO_2) which can be used as nanofiller in polymeric NCs [15]. The MnO_2 has specific features such as high surface area, structural flexibility, natural abundance, environmental friendliness, and inexpensive [16–18]. So far, numerous reports of the different application of MnO_2 have been reported, such as removal of heavy metals [19–22], sensors [23], catalyst [24,25] and energy storage systems [26–28]. Many polymorphous forms have been known for MnO_2 such as α, β, γ, δ, and λ with various morphologies such as nanoparticle, nanowire, nanoflower, nanosheet, nanorod, and nanotube. The basic unit of MnO_2 is the MnO_6 octahedral that linked together in diverse ways. The α-MnO_2 is a (1×1) and (2×2) channeled α-MnO_2 phase with the great surface area and tunnel measure of 0.46 nm [29–33] that make it appropriate for adsorption of heavy metals. The α-MnO_2 nanorods (NRs) tend to cohesion and accumulation, because of high energy surface, small size and electrostatic forces of them. So, surface modification can be suggested for better dispersal and more surface compatibility with the matrix polymer [8,34]. Stearic acid (SA) is a saturated long-chain fatty acid that can be used as a surface modifier, with a graft of its hydrophilic head to the surface of the manganese dioxide.

In the current study, the α-MnO_2-SA NRs were used as nanofiller for the synthesis of blend NCs based on PVA and PVP. The PVA/PVP/α-MnO_2-SA blend NCs (50:50) consisting 1–5 wt% of functionalized α-MnO_2 NRs were prepared via ultrasonic irradiation as a green and effective approach because this approach can provide a clean media and supreme dispersion of nanofiller in a short time. Blend NCs were completely characterized and analyzed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and thermal gravimetric analysis (TGA). The observation of FT-IR and XRD confirmed the synthesis of blend NCs. The FE-SEM and TEM studies indicated that functionalized α-MnO_2 NRs with rod structure were uniformly dispersed in the PVA and PVP matrices. The thermal stability of blend NCs was improved with increasing α-MnO_2-SA quantity, and onset degradation temperature of blend NCs increased about 300 °C in comparison with neat PVA and PVP. The prepared blend NC showed good adsorption of Cd^{II} ion from an aqueous system with q_m of 47 (mg g^{-1}).

2. Materials and methods

2.1. Materials

PVP with the medium molecular weight of 25,000 g mol^{-1}, PVA with a hydrolysis amount of 99% and medium molecular weight of 145,000 g mol^{-1}, manganese (II) sulfate monohydrate ($MnSO_4 \cdot H_2O$) and stearic acid were obtained from Merck Chemical Co. (Germany). Potassium permanganate ($KMnO_4$) was acquired from Sigma-Aldrich (Germany). Cadmium-nitrate-4-hydrate ($Cd(NO_3)_2 \cdot 4H_2O$) was attained from Riedel-de Haen (Germany).

2.2. Characterization

The X-ray diffraction templates were entered by applying a Philips X'Pert MPD X-ray diffractometer (Germany) with Cu Kα beam ($\lambda = 1.54$ A°) within 10-100°. The functional groups of samples were examined by FT-IR (Jasco-680, Japan) within ranges of 400–4000 cm^{-1}. Thermal stability of the samples was studied by recording TGA (STA503 TA, Germany) under argon environment with the heating rate of 20 °C/min. The surface morphology of samples was pursued by FE-SEM (Hitachi S-4160, Japan). TEM analysis was applied to examine fine details using a Philips CM 120 microscope (Netherlands). Fabrication of blend NC films was accomplished using a

probe of Topsonic homogenizer ultrasonic with the power of 100 W and frequency of 20 kHz (IRI). The cadmium ion concentrations were characterized by the Perkin-Elmer 2380-Waltham flame atomic absorption spectrophotometer (FAAS).

2.3. Synthesis of α-MnO_2 NRs

The α-MnO_2 NRs were provided using a hydrothermal system. The detail of procedure: 0.2 g of $MnSO_4 \cdot H_2O$ and 0.5 g of $KMnO_4$ with 1:2.5 mol ratio (dissolved in deionized water) were mechanically mixed for 0.5 h. Subsequently, the solution was transmitted into a sealed autoclave with Teflon-lined and was retained for 12 h at 140 °C. Then, the brown resultant sediments were stacked up by centrifugation and rinsed with deionized water severally in order to removal of residual ions, and dried for 24 h at room temperature (RT) [33].

2.4. Modification of α-MnO_2 NRs with SA

The α-MnO_2 NRs (0.017 g) were dispersed in ethanol (5 mL) under ultrasonic irradiation for 15 min. SA (0.28 g, 4 mmol) was dissolved in ethanol (20 mL) and was added to the α-MnO_2 NRs suspension. The mixture was taken into a sealed Teflon-lined autoclave, followed by a solvothermal reaction at 100 °C for 6 h. After the autoclave was naturally cooled to RT, the resulting precipitate was stacked up by centrifugation, rinsed several times with excess ethanol and deionized water and dried overnight at 60 °C in air [35].

2.5. Synthesis of PVA/PVP/α-MnO_2-SA blend NCs

The PVA/PVP (50:50) blend NC films reinforced with α-MnO_2-SA NRs were synthesized through solvent casting technique with assistance of ultrasonic irradiation. First, PVA (0.1 g) was dissolved in deionized water (8 mL) at 95 °C; then, ultrasonicated for 5 min. Powdered PVP (0.1 g) was dissolved in deionized water (5 mL) and sonicated for 5 min followed by adding to the PVA solution. Then certain amounts of α-MnO_2-SA NRs (1, 3, and 5 wt%) were dispersed in 6 mL of ethanol using stirring for l h and ultrasonicated for 15 min. Next, α-MnO_2-SA NRs suspensions were added to the PVA/PVP solution. The combination was stirred for 24 h at RT but good dispersion was not obtained. Eventually, it was sonicated for 45 min with the frequency of 20 kHz and power of 80 W to obtain the homogeneous blend with the good dispersal of α-MnO_2-SA NRs into the polymer matrices. It is noteworthy that ultrasonic process was accomplished with an ultrasonic probe in a water bath and probe horn was directly submerged in the system. Other power (50, 60, 80, and 90 W) and time (15, 30, 45, and 60 min) of ultrasonic were examined. With increasing the ultrasonication power of 80 W and ultrasonication time of 45 min no changes in dispersion were observed. At lower ultrasonication power of 80 W and lower ultrasonication time of 45 min a homogeneous blend with fine dispersion was not achieved. So, 45 min, as well as 80 W were selected as optimum time and power, respectively. The blend NC films of PVA/PVP/α-MnO_2-SA were obtained with the gradual evaporation of solvent at RT (Fig. 1).

2.6. Adsorption experiment

The efficacy of primary metal ion concentration on Cd^{II} ion adsorption was investigated. Typically, 0.02 g of PVA/PVP/α-MnO_2-SA blend NC 5 wt% was added into each flask containing 10 mL of Cd^{II} ion solutions with various initial metal ion concentrations (20–100 mg L^{-1}) at neutral pH and RT. All flasks were stirred on a shaker table for 20 h at a speed 150 rpm. After the adsorption reached to equilibrium, blend NC was separated by filtration. The extant concentration of Cd^{II} ion was specified via FAAS. The quantity of Cd^{II} ion adsorption in equilibrium and the removal percentage of Cd^{II} ion were assessed from the following Eqs. (1) and (2), respectively.