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Free emulsion polymerization of styrene/layered double hydroxide nanocomposite for Cd and Pb (II) ions removal from aqueous media

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ABSTRACT

This study aims to prepare and characterize of polystyrene/Zn-Al layered double hydroxide (LDH) nanocomposites. In addition to the adsorption capacity of the prepared nanocomposites was evaluated using Cd^{2+} and Pb^{2+} heavy metal ions. The synthesized nanocomposites were prepared using styrene monomer via in situ free emulsion polymerization. The prepared polymeric nanocomposites were characterized using FT-IR, XR D, TEM, and TGA. The prepared nanocomposites were investigated as adsorbent to remove both of Cd and Pb (II) from aqueous media using atomic adsorption spectrometry. The results showed that the high concentration of LDHs exhibited high adsorption efficiency.

KEYWORDS

Layer double hydroxide;
Nanocomposites;
Heavy metal ions;
Polystyrene.

INTRODUCTION

The application of nanotechnology for the remediation of contaminants may give promising results in future. The search for new and advanced materials is an important task of contemporary research in the environmental protection. In recent years, a great deal of attentions has been focused onto the application of nanostructured materials as adsorbents or catalysts to remove toxic and harmful substances from wastewater and air[1,2]. These Materials with high adsorption capacities are very attractive from an economical point of view. Among these the Layered Double Hydroxides (LDHs), also known as hydrotalcites (HTs) or anionic clays, have also deserved interest, due to their large ionic exchange capacities (3.3 meq/g in comparison to 1 meq/g in cationic clays)[3]. The use of hydrotalcites, for the purification of water is well understood and progress today is mainly in improving the efficiency and specificity of the HTs and their applications[4]. Layered double hydroxides (LDHs), as hydrotalcite (HT)-like materials, are a class of synthetic two-dimensional nanostructured anionic clays whose structure can be described as containing brucite-like layers, where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been replaced isomorphously by trivalent cations, which giving positively charged layers with charge-balancing anions between them; where some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region[5]. LDHs may be represented by the general formula $[M^{2+}_{1–x}M^{3+}_{x}(OH)_2]^{x+}(A^{n–})_{x/n} \cdot mH_2O$, where M^{2+} (M = e.g. Mg, Fe, Co, Cu, Ni, or Zn) and M^{3+} (M = e.g. Al, Cr, Ga, Mn or Fe) are di- and trivalent cations respectively; the value of x is equal to the molar ratio of M2+/(M^{2+} + M^{3+}) and is generally in the range 0.2–0.33; $A^{n–}$ is an anion. Layered double hydroxides have certain specific advantages over conventional nanofillers as summarized by Costa *et al*[4]. At present, a different kind of layered inorganic material, generally called LDH, is also gaining importance as nanofiller for the synthesis of polymer nanocomposites. These materials have a very wide range of chemical compositions based on different metal species, interlayer anions, etc. and are well known for their catalytic activities in organic synthesis[6]. The other potential applications of LDHs and their modified forms include biomedical applications e.g. controlled release of various drugs and biomolecules[7,8], improvement of heat stability and flame retardancy of polymer composites[9]. Heavy metals are toxic contaminants that must be removed from underground water and wastewater before being discharged to the environment. A wide range of physical and chemical processes are available for the removal of heavy metal ions during wastewater treatment. These include ion exchange, electrochemical precipitation, filtration, and adsorption to commercial activated carbon[10]. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries[11]. The concentration of these metals in wastewater may therefore rise to a level that can be hazardous to human health, livestock and the aquatic environment. Haroun *et al*.[12,13] reported that some renewable materials were potentially utilized for removal some heavy metals from aqueous media due to their low cost and relatively high metals adsorption rate. The present work investigates the preparation and characterization of novel polystyrene/LDHs nanocomposites using free emulsion polymerization using LDHs as emulsifier. Furthermore, the performance of the prepared nanocomposites in waste water treatment which loaded with several heavy metal ions such as: cadmium and lead has been studied.

MATERIALS AND METHODS

Materials

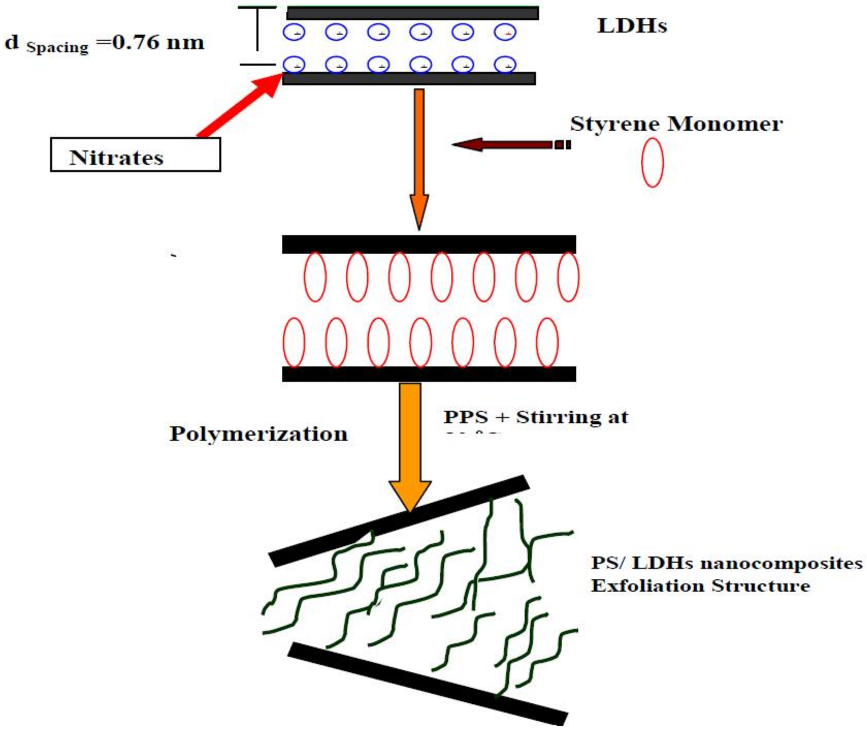
Styrene monomer (C_8H_8, Aldrich) and potassium persulfate as initiator (PPS, $K_2S_2O_8$, Reanal, Hungary) was used to prepare the polymer samples (were used to achieve free surfactant emulsion polymerization). For the preparation of 2:1 Zn/Al LDH, Zn-acetate ($C_4H_6O_4Zn \cdot 2H_2O$, Puriss, Reanal, Hungary), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Puriss, Molar, Hungary) and sodium nitrate $NaNO_3$ (Puriss, Reanal) precursors were used with sodium hydroxide NaOH (Molar, Hungary).

Preparation of Zn/Al LDHs

The double layered hydroxide was synthesized according to Hornok *et al*.[14] and Patzkó *et al*.[15]. Prior to preparation carbonate-free distilled water was obtained by boiling and N_2-bubbling through the cooled water. In the case of 2:1 (Zn/Al) composition, the Al-nitrate solution containing 37.5 g of solute and 600 ml of water was stirred in a three-necked round flask while the Zn-salt solution (43.8 g in 600 ml) was poured to the above described solution. Then the solution of NaOH (28.0 g) in excess, and sodium nitrate $NaNO_3$ (20.0 g) in 2800 ml of carbonate-free distilled water was slowly added (within 10 minutes) to the precursor containing mixture during vigorous stirring and in N_2 atmosphere. The white dispersion was heated to 60°C and left for 5 hours. The precipitate was then aged for 14 hr at ambient temperature. The dispersion was collected and washed till pH 8-9. The resulting materials were dried at 60°C and kept for further investigations.

Preparation of the nanocomposites

The polymeric nanocomposites were prepared *via* free emulsion polymerization. Typically, in a 250 ml three neck flask using different concentrations of LDHs (Zn/Al 2:1) and styrene monomer (0.2, 0.4, 0.6 and 0.8) %. They were dispersed in 100 ml deionized water then the mixture was sonicated for 30 min for well dispersion of LDHs in the aqueous media. 0.1 mg of PPS (as an initiator) was added into the mixture, then the flask was immersed in a water bath at 70°C under a magnetic stirring (750 rpm) and the polymerization was instantly initiated and the reaction leave under stirring for 8 hr as shown in Scheme 1. The samples were precipitated using ethanol and deionized water as well as it was filtered and dried at 60°C to get the final product.



Scheme 1 : Schematic pathways of in-situ free emulsion polymerization within LDH layers to synthesize polymer/LDH nanocomposites.

Characterization

The XRD patterns of the prepared materials were carried out in a Bruker D8 Advance X-ray diffractometer with CuK_α radiation (λ= 0.1542 nm, 40 kV, 30 mA). The lattice d-spacing was calculated from the reflections in the diffraction patterns via Bragg's equation. The thermal gravimetric analysis (TGA) was carried out under a N_2 atmosphere at a heating rate of 10^{o}C/min, for knowing their thermal stabilities. The transmission electron micrographs were taken in Philips CM-10 transmission electron microscope (TEM) with an accelerating voltage of about 100 kV.

Adsorption study of Cd (II) and Pb (II) ions

Quantitative determination of Cd (II) and Pb (II) were conducted using atomic absorption spectrometer. Thermo atomic absorption spectrometer with hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air acetylene flame. Calibration standards were regularly performed to evaluate the accuracy of the analytical method. Working calibration standards of Cd (II) and Pb (II) were prepared by serial dilution of concentrated stock solution. LDHs nanocomposites adsorbent were tried to determine their efficiency to remove heavy toxic metals from artificial wastewater by column elution technique. Glass column (30 cm x 1.8 cm) were taken and plugged with cotton. LDHs nanocomposites (1 g) was loaded into the column and was washed with 25 ml distilled water. Water sample (100 ml) was fortified with Cd^{2+} and Pb^{2+} mgL^{-1} level and passed through the column. Flow rate was adjusted at 5 ml min^{-1}. The elute was collected in a beaker. 10 ml fraction was taken and the metals were determined by atomic absorption spectrophotometer. Furthermore, blank (without adsorbent) was simultaneously processed to determine the metal loss during processing. The removal efficiency of adsorbent was calculated by eliminating the contribution due to processing. Each sample was done in triplicate to confirm the data.

RESULTS AND DISCUSSIONS

Characterization of the prepared nanocomposites

Figure 1 shows FTIR spectra of Zn/Al LDHs as will as pure PS and PS-Zn/Al (4%) nanocomposites, respectively. FTIR spectrum of the polystyrene Zn/Al

LDH nanocomposites was shown clearly the characteristic absorptions attributable to both the polymeric organic and inorganic groups. This indicates that the Zn/Al LDH are dispersed into the polystyrene matrix to form the PS-Zn/Al LDH nanocomposites. The pure polystyrene have several characteristic absorption bands at 3070 and 3030 cm^{-1} (aromatic C-H stretching), 2960 and 2930 cm^{-1} (aliphatic C-H stretching), 2000-1680 cm^{-1} (weak aromatic overtone and combination band), 15 04 and 1496 cm^{-1} (C=C stretching), 1453 and 1368 cm^{-1} (CH$_2$ bending), 757 and 698 cm^{-1} (C-H out-of-plane bending of phenyl ring or mono substituted benzene). The X-ray diffraction pattern of the Zn/Al LDHs established the successful preparation of layer double hydroxide as shown in Figure 2a. The LDH possesses the diffraction peaks characteristic of LDH and ZnO, while reflections refer to the intercalation appears at lower 2θ°. The interlamellar distance was 0.76 nm, the obtained interlayer space corresponds to the perpendicular arrangement of nitrates groups between the LDHs lamella. Whereas after the polymerization of styrene monomer by in situ free emulsion polymerization using PPS as initiator in absence of any emulsifier at 70^{o}C, and different concentration of Zn/Al-LDHs. Firstly, the intercalation of monomer molecules into the LDHs lamellae then the polymerization take place and the exfoliation nanocomposites will predominate by using different loadings of LDHs (Figure 2 c, d, e, f) contrasted to the pure LDHs and pure polystyrene. The thermal stability of the prepared LDHs as well as PS/LDHs nanocomposites were revealed in Figure 3 and TABLE 1, the loss of adsorbed water emerges at lower temperature, while the peak around 400°C indicates the decomposition of the polymer, and the peaks show at somewhat lower temperature relative to the pure polymer. The peak at 489°C shifts to higher temperature range in the high LDHs concentration (8%). Supplementary information concerning the thermal behavior of the nanocomposites loaded with 2-8% of LDHs, as representatives of the prepared polystyrene nanocomposites is showed in Figure 3. It can be found that the existence of the layered double hydroxide, even in their un-organophilized form, enhanced the thermal stability of the polystyrene nanocomposites, which strongly indicates that on contrary to other particulate inorganic filling materials they played a pronounced role in the thermal stability, acted more effectively upon increasing the loading to 8%. This is a typical behavior of the elements possessing tubular or platelet–like structures which increase the thermal stability of the prepared nanocomposites. Figure 4 shows TEM of the prepared Zn/Al LDH based nanocomposites with different LDH concentrations. The morphology of the sample particles is sphere-like in shape with different nanometer size diameters ranging from 70-80 nanometers. Thus the most important contribution of building polystyrene layered double hydroxide adsorbent with hierarchical architecture is the enhance of sensitivity it generates, owing to the large surface area of LDHs. Furthermore, Figure 4 illustrated that the important of LDHs bridging between polystyrene nano-beads that can explain the disconnection of the conducting network connections appear to be appreciative paths for adsorption of heavy metals.

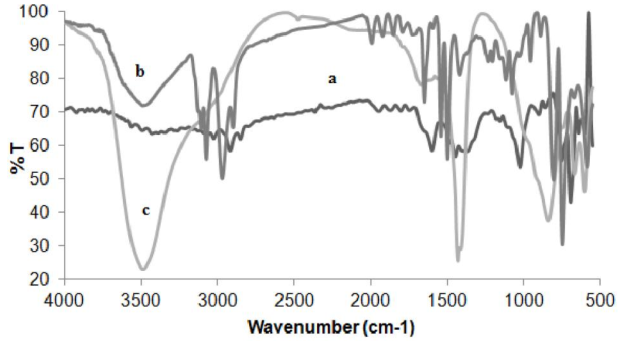


Figure 1 : FT-IR spectra of (a) PS, (b) 4% LDH and (c) Zn/Al-LDH (2:1).

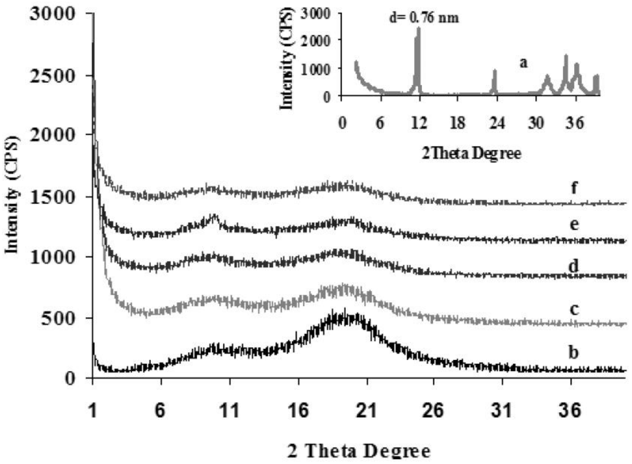


Figure 2 : XRD of Zn/Al-LDH (2:1) as well as polystyrene prepared by emulsion polymerization and PS/ LDHs nanocomposites prepared by free emulsion polymerization using PPS as initiator in absence of any emulsifier at 80 ^{o}C, and different concentration of Zn/Al-LDHs a) Zn/Al (2:1) LDH, b) pure PS, c) 2%, d) 4%, e) 6% and f) 8%.

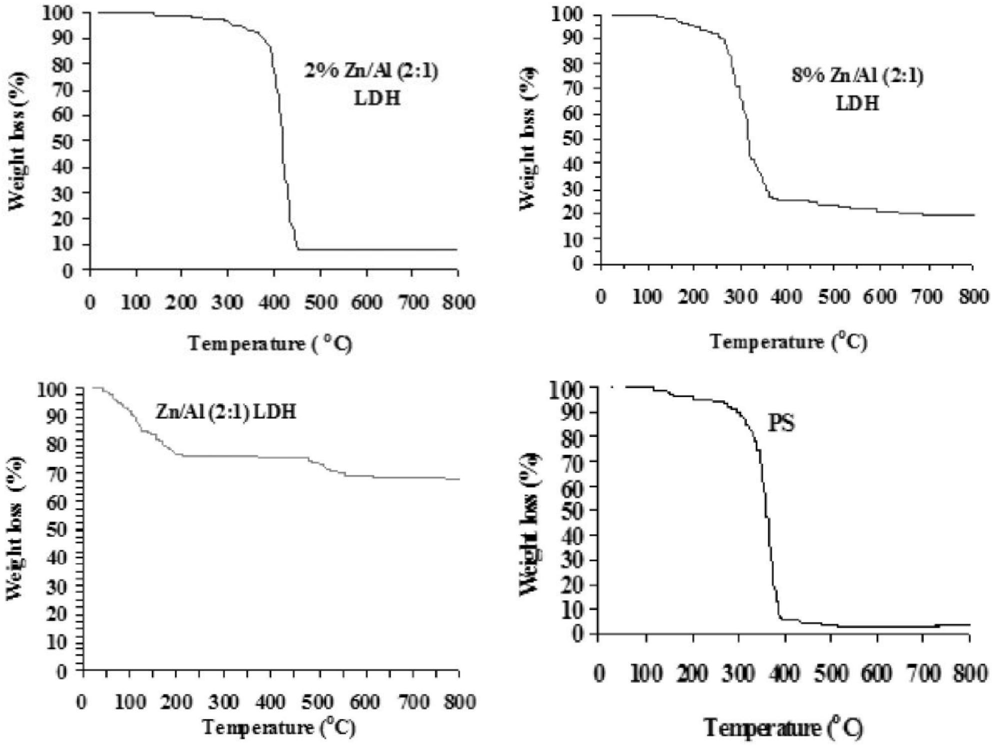


Figure 3 : TGA of Zn/Al (2:1) LDH as well as pure polystyrene and PS/LDHs prepared by free emulsion polymerization using PPS as intiator and stirring for 6 hr. at 80 °C with different concentration of Zn/Al (2:1) LDH.

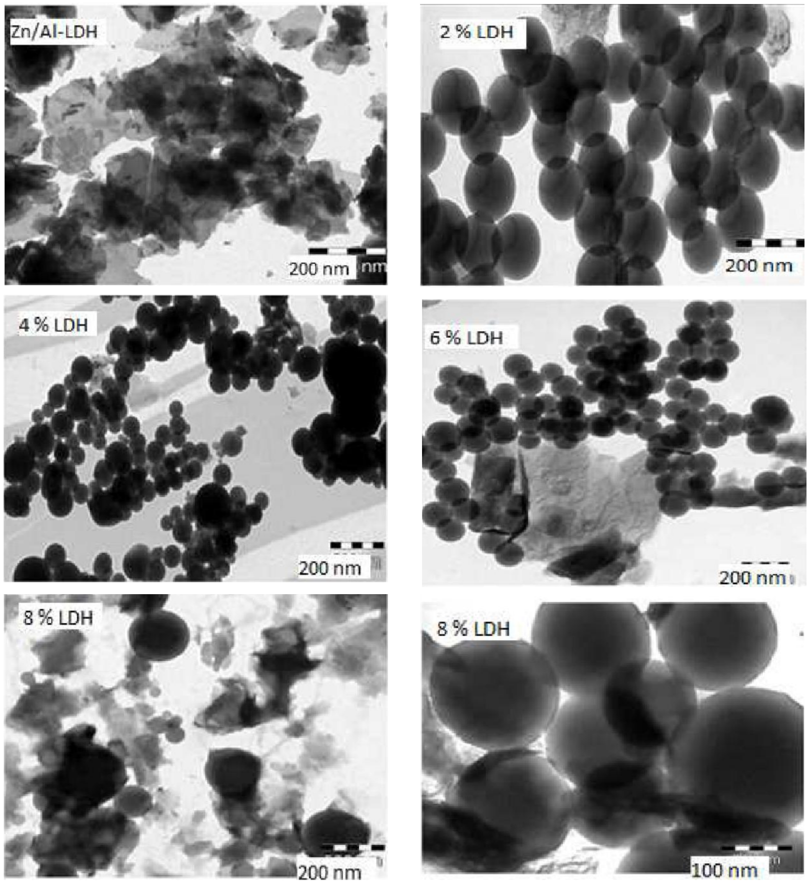


Figure 4 : TEM of the prepared Zn/Al LDH based nanocomposites with different LDH concentrations.

TABLE 1 : TGA data of the prepared nanocomposites

Nanocomposites	Weight loss (%) at different temperatures (°C)		
	67-210 (°C)	210-489 (°C)	489-623 (°C)
Zn/Al (2:1) LDH	1.7	4.0	28.3
PS	1.5	7.5	95
2% LDH	---	94	---
8% LDH	---	85	---

Adsorption uptake of Cd and Pb (II) ions

Heavy metals, when in considerable concentrations in water that may pretense harmful health effects. That includes lead, silver, mercury, copper, nickel, chromium, zinc, cadmium and tin that must be removed to certain levels to meet discharge requirements. The possible adsorption mechanism of Cd (II) and Pb (II) with LDH-based nanocomposites has unknown yet presently. Further studies should be carried out to exploit the mechanisms for the assembly in remediation applications. Obviously, the removal of heavy metal ions of Cd^{2+} and Pb^{2+} by the assembly was not a single process, mainly controlled by the isomorphic substitution, coupled with the adsorption bonding with surface hydroxyl groups and surface precipitation[16]. TABLE 2 shows the final removal efficiencies of Cd^{2+} and Pb^{2+} ions from aqueous media. It can be seen that the removal percentages were increased with an increasing of LDHs concentration till 4%. Moreover, the removal percentages were decreased when LDH concentration above 6%. This may be due to the anion competition for binding sites such as $(CO_3)^{-2}$ and $(HPO_4)^{-2}$, which are present in ground water, decrease overall sorption capacities of LDH, especially at higher LDHs concentration than 4%. This may explain why the sorption capacity of LDH-based nanocomposites was decreased at LDH concentration 4%.

TABLE 2 : The effect of the LDH concentration on the percentage of the Cd and Pb (II) removal from aqueous media.

LDH Concentrations (%)	Heavy metals removal percentages (%)	
	Cd (II)	Pb (II)
2	51	33
4	74	95
6	25	59
8	47	81

CONCLUSIONS

Zn/Al (2:1) LDHs were successfully prepared and confirmed using XRD and FTIR spectroscopy. They could be used as filler and surfactant at the same time during the *in situ* free emulsion polymerization of styrene monomer. The prepared polystyrene nanocomposites exhibited spherical-like in shape with nanometer particles size. Moreover, the prepared polystyrene/layer double hydroxide nanocomposites showed high thermal stability more than that of the pure polystyrene using thermal gravimetric analysis TGA. Furthermore, the prepared polystyrene nanocomposites had high performance for removal of heavy metal ions such as: Cd^{2+} and Pb^{2+} from aqueous media. They exhibited remarkably high adsorption capacities for removal of Cd^{2+} and Pb^{2+} ions about 74 and 95 %, respectively.

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