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Fabrication of MWCNTs/ThO_2 nanocomposite and its adsorption behavior for the removal of Pb(II) metal from aqueous medium

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ABSTRACT

Multiwall carbon nanotubes (MWCNTs) were chemically modified to form nanocomposite with thorium oxide. The MWCNTs/ThO_2 nanocomposite was characterized using different modern techniques including Fourier transform infrared spectroscopy, X-ray powdered diffraction, scanning electron microscope, and transmission electron microscope. The average size of MWCNTs/ThO_2 nanocomposite was in the range from 5 to 10 nm. The nanocomposite material was investigated for its adsorption behavior for Pb(II) ions removal from its aqueous system. For the adsorption of Pb(II) by MWCNTs/ThO_2, the equilibrium was achieved within 50 min. The temperature and pH have also found to play important role in the adsorption process and maximum adsorption was found at 45˚C and pH 5.5.

Keywords: Multiwall carbon nanotubes; Nanocomposite; Pb(II) metal; Adsorption

1. Introduction

Heavy metal pollution is one of the most concerned issues at the present time. Heavy metals not only persist in the environment for longer duration but also bioaccumulate in living beings [1–3]. The main environmentally concerned heavy metals are cadmium, arsenic, nickel, chromium, copper, lead, and cobalt [4–6]. Among these metal ions, Pb(II) is one of the most dangerous heavy metals released every day in environment from diverse sources including mining and smelting process, combustion of fossil fuels, paints, batteries, untreated dumping of Pb(II) compounds [7,8]. Hence, the prime need of the time is to remove and recover Pb(II) metal ions from biotic and abiotic systems and create a lead-free environment.

It has been well established now that even traces of Pb(II) give significant physiological and neurological effects in humans [9]. The maximum tolerable limit of Pb(II) in drinking water is 0.1–0.05 mg L^{-1} [10,11]. The major health problems associated with Pb(II) are nephrotoxicity, neurotoxicity, hypertension, damage to central nervous system, cognitive deficits in children, etc.

There are various techniques in use for the removal of various types of metal ions but the adsorption is considered one of the most efficient, versatile, and inexpensive processes [12–17]. In recent past, diverse adsorbents have been explored for the adsorption of Pb(II), some of the important adsorbents are

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calcium phosphate-based materials, chitosan pyruvic acid derivatives, activated carbons, agricultural wastes, biochars, magnetic hydroxyapatite/Fe_3O_4 microspheres etc., but most of these adsorbents are carbon based. The discovery of multiwall carbon nanotubes (CNT) as one of the promising adsorbent materials has been major breakthrough in this research area and the material has been explored as advanced candidate for the remediation of harmful organic and inorganic pollutants from different mediums [18–21]. The promising properties of CNTs include large surface area, layered structures, greater mechanical strength, high thermal and chemical resistivity [22]. Functionalization of CNT is an important task which makes them highly specific and selective in nature and also increases their dispersity [23]. Their high surface area and strong interactions with adsorbate enhance their applicability for scavenging wide range of pollutants including heavy metals, dyes, and other organic toxic substances [24–26]. The functionalization of CNTs is easily feasible process which is based on introduction of specific functional group(s) such as –COOH, –OH, $–SO_3$, etc. onto the surface of CNT. One of the most promising features of CNTs is their nature to support metallic oxides [27,28].

In the present work, multiwall carbon nanotubes (MWCNTs)/ThO_2 nanocomposite was prepared and characterized using various modern techniques. The material was explored for its adsorption behavior for the removal of Pb(II) ions from its aqueous medium. The effect of various parameters like pH, contact time, initial Pb(II) concentration, and temperature were also carried out for the adsorption of Pb(II) onto MWCNTs/ThO_2.

2. Experimental

2.1. Materials

CWCNTs with diameters of 10–20 nm were obtained from Shenzhen Nanotech Port Co., Ltd and used as received. All other chemicals and regents used in this study were from M/s Sigma Aldrich, Germany and analytical reagent grade.

2.2. Fabrication of MWCNTs/ThO_2

For the synthesis of MWCNTs/ThO_2 nanocomposite, 0.5-g MWCNTs were treated with 100 mL of HNO_3 (68%) for 24 h at 70˚C, then washed with water and dried in an oven at 60˚C for 12 h. Two hundred fifty milligrams of acid-treated carbon nanotubes were magnetically stirred and 50 mL of thorium nitrate solution of known concentration was added dropwise into the dispersed MWCNTs. Afterward, the suspension was dried at 150˚C. The obtained material was heated up to 400˚C for 2 h and the resulted product was designated as MWCNTs/ThO_2 nanocomposite.

2.3. Characterization techniques

The MWCNTs/ThO_2 nanocomposite was characterized using various techniques including scanning electron microscope (SEM) (JSM-6380 LA, Tokyo, Japan), transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan), X-ray powdered diffraction (XRD) (Shimadzu XRD Model 6000), and Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, Thermo Scientific, USA).

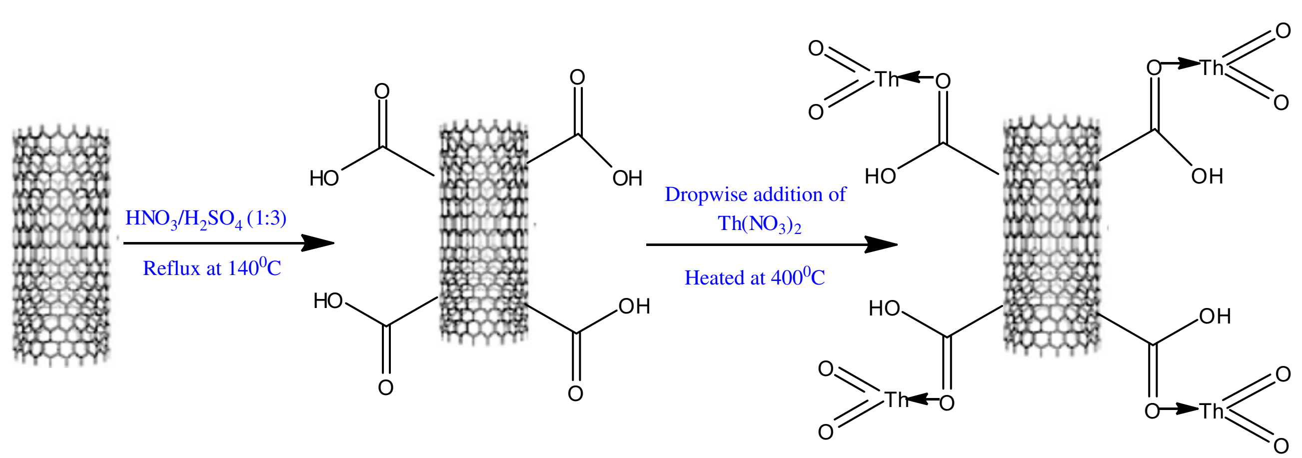

Fig. 1. Synthesis of MWCNTs/ThO_2 nanocomposite.

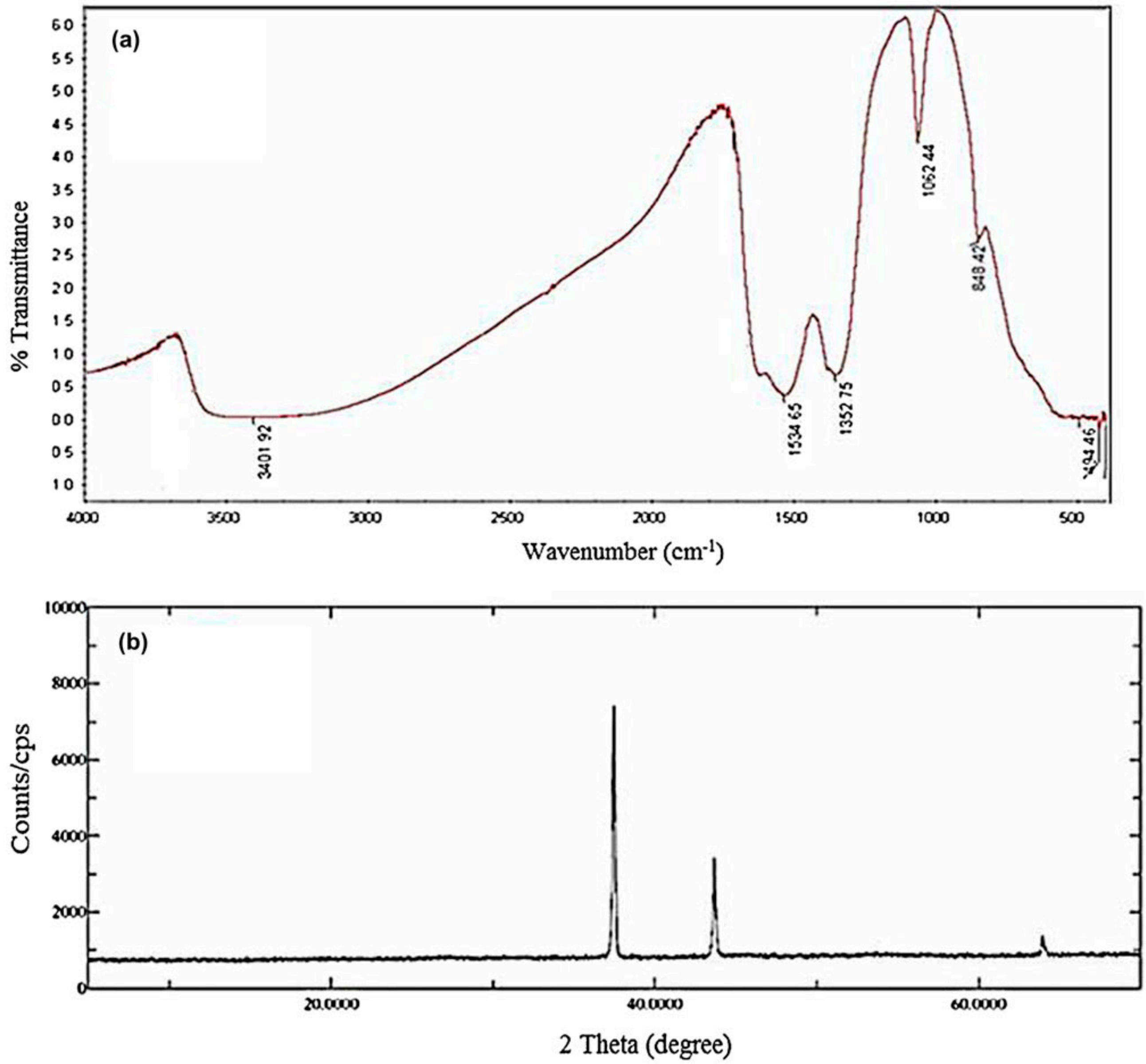

Fig. 2. (a) FTIR Spectra and (b) XRD Pattern of MWCNTs/ThO_2 nanocomposite.

2.4. Adsorption experiments

The adsorption behavior of MWCNTs/ThO_2 was studied for Pb(II) ions removal from aqueous medium using batch process. The 20 mg of MWCNTs/ThO_2 was added to 100 mL of Pb(II) ion solution in a 250-ml conical flask and effects of different experimental parameters such as contact time, temperature, pH of solution, and time interval were studied. The flasks solution was kept well closed with stopper and then shaken at 100 rpm in a shaker fitted with water bath at appropriate temperature. All the experiments were performed in triplicates to obtained mean value. The MWCNTs/ThO_2 was removed from test solution by centrifugation method. The initial and final concentrations of metal ions in test solutions were determined by using atomic adsorption spectroscopy (AAS). The adsorption behavior and capacity of MWCNTs/ThO_2 were determined. The results were expressed as percentage removal (%) of Pb(II) ions. The adsorption capacity was determined as [29]:

$$q_e = \frac{V(C_o - C_e)}{m} \tag{1}$$

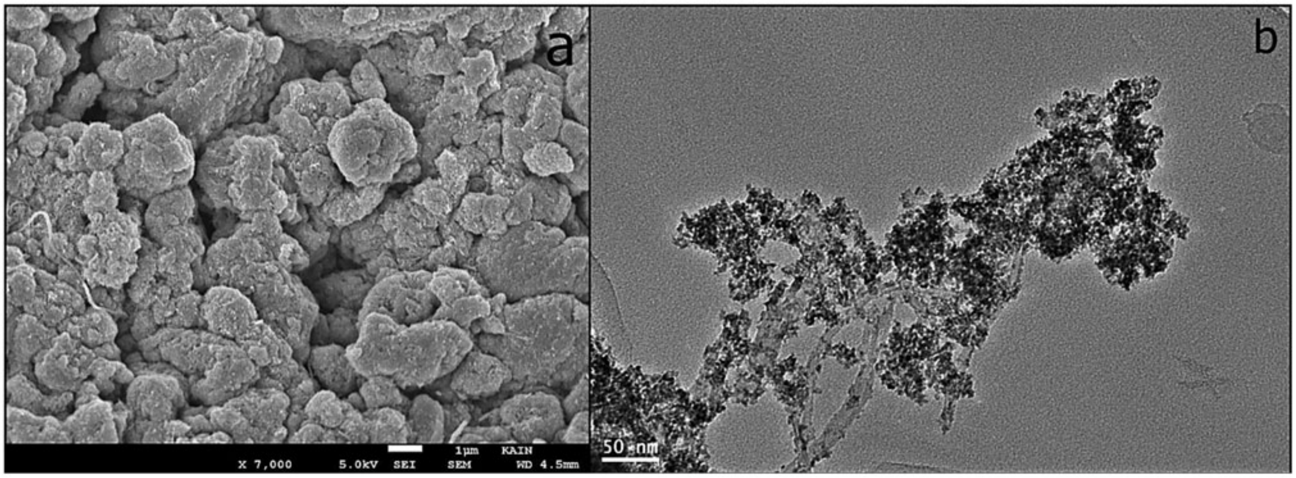

Fig. 3. (a) SEM Micrograph and (b) TEM Micrograph of MWCNTs/ThO_2 nanocomposite.

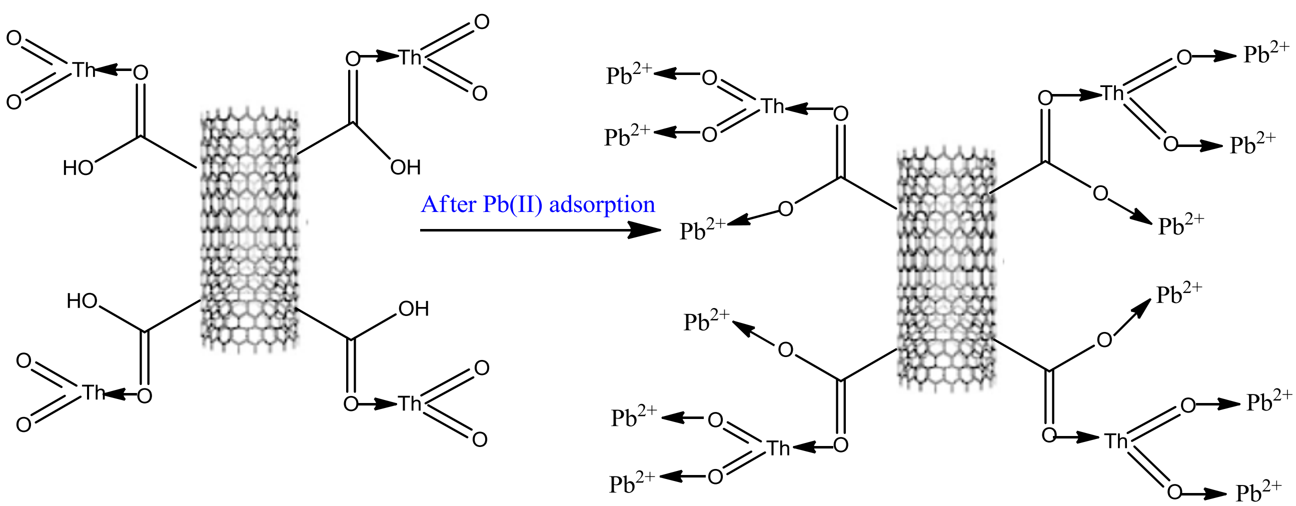

Fig. 4. Mechanism for the Adsorption of Pb(II) onto MWCNTs/ThO_2 nanocomposite.

where q_e (mg g^{-1}) is the amount of metal ions adsorbed on adsorbent, V (mL) is the volume of metal ion solution, C_o and C_e are the initial and equilibrium concentrations of metal ions in the solution phase, respectively, and m is the mass of adsorbent. During the course of the study, the contact time was varied from 2 to 90 min, the solution pH from 2 to 6, initial Pb(II) concentration from 5 to 75 mg L^{-1} and the temperature was raised from 25 to 55℃.

3. Results and discussion

The MWCNTs were modified into MWCNTs/ThO_2 nanocomposite using simple chemical method. The detail method for the synthesis is shown in Fig. 1. The modified MWCNTs were well characterized to understand the physicochemical properties. The FTIR spectrum of MWCNTs/ThO_2 is given in Fig. 2(a), representing prominent peaks in different regions. The characteristic broad peak observed in the range of 3,400–3,700 cm^{-1}, corresponds to –OH group stretching vibrations, indicating thereby presences of the hydroxyl groups in the matrix of the nanocomposites [30]. The peak at 1,352.75 cm^{-1} is due to the presence of atmospheric CO_2. The presence of peak at 1,062.44 cm^{-1} is probably due to the result of C–O stretching frequency [31]. The absorption band at 494.46 cm^{-1} corresponds to asymmetric M–O stretching vibration of metal oxide linkage [32].

For X-ray diffraction analysis of MWCNTs/ThO_2, manganese-filtered CuK_α radiation wavelength (l50.1542 nm) at 298 K was used. The instrument was equipped with graphite monochromator, operating at 40 kV and 30 mA. Fig. 2(b) exhibits the diffractogram of MWCNTs/ThO_2 and indicates sharp peaks at 2θ around 38˚ and 42˚, confirming the crystalline nature of MWCNTs/ThO_2. SEM image (Fig. 3(a)) of the MWCNTs/ThO_2 nanocomposites illustrates an entangled network of oxidized MWCNTs with clusters of thorium oxides attached to them, indicating thereby the formation of MWCNTs/ThO_2 oxide nanocomposites. The TEM studies revealed that MWCNTs/ThO_2 nanocomposite lies in the nanorange 5–10 nm (Fig. 3(b)).

The practical applicability of MWCNTs/ThO_2 was performed for the adsorption of Pb(II) from aqueous medium. The high adsorption of Pb(II) onto MWCNTs/ThO_2 might be due to the presence of various oxygen atoms of thorium oxide as well as carboxylic group, which have free lone pair of electrons and make the coordinate bond with the electropositive Pb(II) metal ion (Fig. 4). The removal of Pb(II) as a function of contact time is given in Fig. 5(a) which shows that the adsorption of Pb(II) initially increased rapidly and the equilibrium was achieved in 50 min at adsorption efficiency of 93.5%. Though the highest value of Pb(II) adsorption by MWCNTs/ThO_2 was attained at 90 min (93.8%), there was not much difference between obtained data for 50 and 90 min. So the contact time 50 min was selected for all further studies.

The pH is one of the most significant environmental factors affecting not only site dissociation but also the solution chemistry of the heavy metal ions [33,34]. It can be seen from Fig. 5(b) that the Pb(II) adsorption is low in the acidic medium. As the pH increases from 2 to 5.5, the adsorption also increases and maximum adsorption of Pb(II) (94.6%) is achieved at pH 5.5. Under acidic conditions, the low adsorption can be explained due to increase in positive charge (protons) density on the surface sites of MWCNTs/ThO_2 and thus, electrostatic repulsion occurs between the Pb(II) ions and the positive surface of MWCNTs/ThO_2. However, with increasing pH, the competition from the H^+ decreases and the positively charged Pb(II) ions can be adsorbed at the negatively charged sites of the MWCNTs/ThO_2 [35,36]. On the other hand, above pH 5.5, Pb(II) starts precipitating as $Pb(OH)_2$ and hence studies in this range could not be conducted.

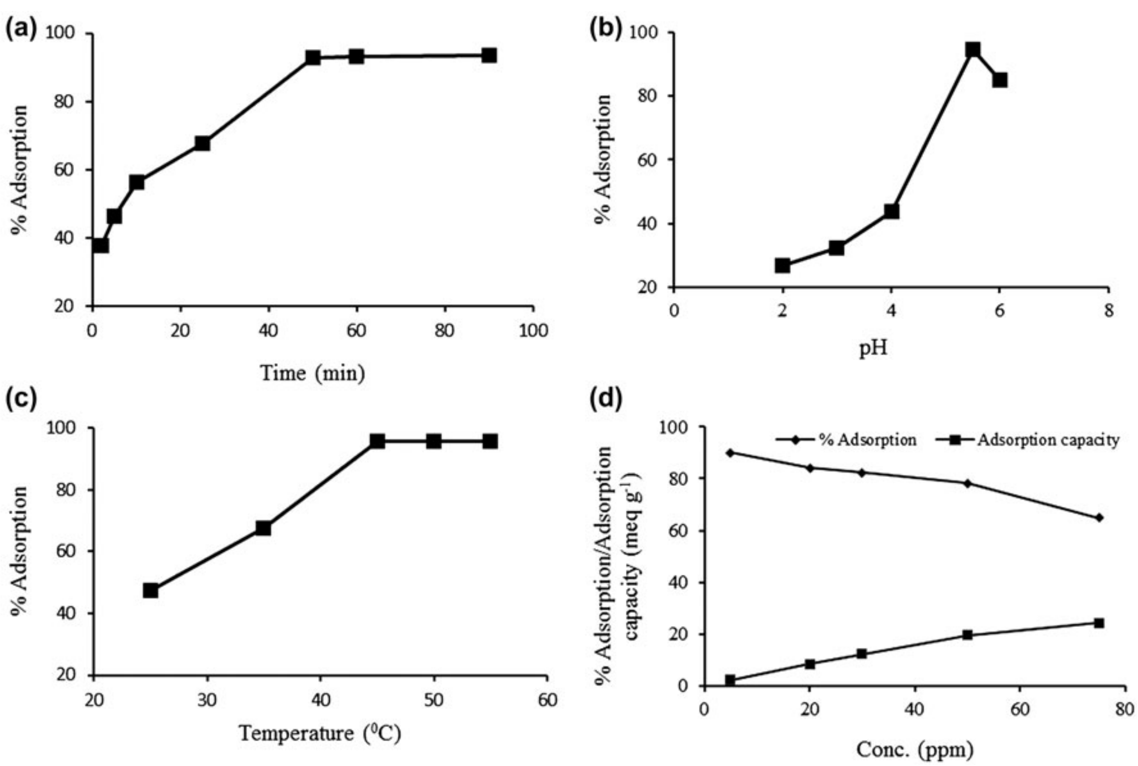

Fig. 5. Adsorption of Pb(II) onto MWCNTs/ThO_2 at Different: (a) contact time, (b) pH, (c) temperature, and (d) Initial Pb(II) concentration.

The temperature at which adsorption process is carried out can affect both the adsorption rates as well as the adsorption capacity of the adsorbents. The effect of temperature on the adsorption of Pb(II) onto MWCNTs/ThO_2 was observed at pH 5.5 and contact time 50 min. The adsorption was found to increase with increasing temperature, thereby indicating the endothermic nature of Pb(II) adsorption onto MWCNTs/ThO_2 [37–39]. At 25˚C, the adsorption of Pb (II) was only 47.3%, while it was increased up to 95.5% at 45˚C and after that it became constant (Fig. 5(c)). To study the effect of initial Pb(II) concentration on the adsorptive removal of Pb(II) by MWCNTs/ThO_2, the initial Pb(II) concentration was varied between 5 and 75 mg L^{-1}, whereas the MWCNTs/ThO_2 dosage was maintained 200 mg L^{-1}. As given in Fig. 5(d), the adsorption capacity was raised with the increase in Pb (II) ion concentration, which might be due to the high driving force for mass transfer at higher concentrations and greater utilization of available adsorption surface and active sites [40,41].

4. Conclusion

The MWCNTs were chemically modified to form nanocomposite with thorium oxide and characterized using various analytical techniques. This the MWCNTs/ThO_2 composite was effectively used for the removal of a highly toxic Pb(II) metal from aqueous medium. The highest adsorption was observed at pH 5.5 and 45˚C. The adsorption was endothermic as it increased with the increasing in temperature. The adsorption of Pb(II) onto the MWCNTs/ThO_2 was due to the removal of H^+ of the MWCNTs/ThO_2 by Pb(II) metal ions. The use of MWCNTs/ThO_2 adsorbents may be a potential candidate for the treatment of liquid wastes containing toxic Pb(II) metal ion.

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