

Poly(vinyl alcohol)-Based MWCNT Hydrogel for Lead Ion Removal from Contaminated Water

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ABSTRACT: In this article, we are discussing the synthesis and characterization of poly(vinyl alcohol)-based multiwalled carbon nanotubes (MWCNT) hydrogels and its evaluation studies for toxic metal ion removal. The functionalized MWCNT serves the purpose of toxic ion adsorbent and PVA is functioning as the substrate for the stable dispersion of MWCNT. We have carried out the evaluation studies using lead ions Pb(II) in batch experimental mode. The percentage removal of Pb(II) was examined by varying experimental conditions viz. dosage of adsorbent, pH of the solutions, and contact time. It was found that 80% removal was achieved under optimal conditions. This adsorption potential is

found to be far better than that of simply dispersing MWCNT in water. The equilibrium adsorption follows the Freundlich adsorption isotherm model. After Pb(II) adsorption, the ions were easily desorbed using a high pH solution, completely regenerating for further removal process. This novel approach of dispersing MWCNT in hydrogel and their re-use after desorption is expected to have promising outcome in the water purification application. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E670–E674, 2012

Key words: nanomaterials; multiwalled carbon nanotube; heavy metal ion; adsorption; hydrogel

INTRODUCTION

Clean water is a requirement for human health. This means, one should ensure that the water should be free from any toxic materials and pathogens before drinking. The ground water get contaminated by toxic/harmful metal ions due to various reasons like discharge from municipal coal burning power plants, chemical manufacturing processes, discharge from municipal sources etc.¹ Adsorption is one of the major methods employed for the removal of heavy metal ions from water. Many kinds of adsorbents, such as activated carbon,^{2,3} activated carbon cltohs,⁴ fly ash,⁵ chitin,⁶ prawn shell,⁷ peanut hull pellets,⁸ and resins⁹ have been developed for the removal of heavy metal from water. Presently researchers are focusing on exploiting the use of nanomaterials as adsorbents for water cleanup.¹⁰ Nanomaterials are available today in the form of activated materials like carbon or alumina. The small size of nanomaterials creates a major challenge.¹¹ These fine particles or tubes cannot just be added to drinking water; rather, they must be incorporated

into a substrate that allows for the contaminants to readily come in contact with the active media.

Multiwalled carbon nanotubes (MWCNTs) are introduced recently in water purification applications as an efficient adsorbent and reported for removal of different heavy metal ions like Lead (Pb(II)), Cadmium(Cd(II)), Arsenic(As(III)), Zinc(Zn(II)), Fluoride, etc.^{12–17} The major problem in using MWCNTs is that it tends to agglomerate as bundles due to electrostatic forces and thus they are difficult to disperse. These materials have high surface areas; however, because of the fine pores, not all the water can easily reach the active surfaces and they are easily plugged. Hence, it is reported that the surface oxidation of MWCNT and attachment of functional group improve the dispersivity and specific area of the MWCNTs.¹⁸ After that the functionalized MWCNT is dispersed in heavy metal ion contaminated water and continuously sonicated for fairly long time. The regeneration of this material is not very easy. For making the expensive nanomaterial cost-effective, there should be an alternative for regeneration of the material. Hence, we propose a new method in which MWCNT is dispersed in polymer hydrogel and the material can use for the metal ion adsorption from water. The advantage of this method is that it does not require sonication during the adsorption experiments and also the material can regenerate without much complication.

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MATERIALS AND METHODS

MWCNTs (Diam. 110–170 nm, Length 5–9 micron, Purity >90%) used in the studies were procured from Sigma-Aldrich, India. Poly(vinyl alcohol) (PVA) (M.W. 72,000) was procured from the Merck. All other chemicals used in the experiments were of analytical grade and the product of S.D. Fine chemicals, India. Ultrapure water (Resistivity: 18.2 MOhm.cm, Elix) was used throughout the experiments.

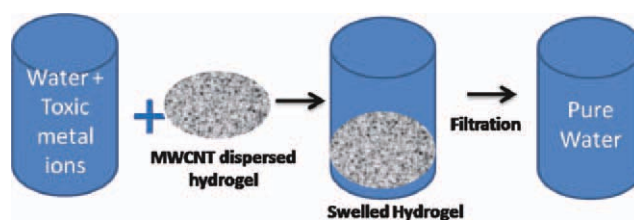
Following a reported procedure, the as-received MWCNTs were first refluxed with a mixture of concentrated sulfuric acid and nitric acid at 80°C for 4 h.¹⁹ Upon completion, the functionalized MWCNTs was added drop wise to cold distilled water and filtered. The filtrant was then washed with distilled water until no residual acid was present. The sample was then dried at 250°C for 3 h. The thermal characterization of the material was carried by thermo gravimetric analysis (TGA) using TA Q-500 instrument in nitrogen atmosphere at a heating rate of 20°C/min.

Preparation of PVA/MWCNT hydrogel

Five percent of PVA solution was made by dissolving appropriate amount of polymer in hot deionized water at 80°C for 2 h using a magnetic stirrer with hot plate. The hydrogel was made by dispersing MWCNT in the aqueous solution of PVA using a mechanical probe sonicator (0.5 inch diameter, maximum power 400 W, frequency 20 kHz; Branson ultrasound 450D, Danbury) followed by crosslinking. About 0.2 g of MWNT was added in to 500 mL of PVA solution and the mixture was sonicated for 5 min, keeping the beaker immersed in cold water. 10 mL of 2.5% glutaraldehyde solution and 1% HCl, which act as the cross linking agent and catalyst, respectively,²⁰ was added to the above solution followed by sonication for 2 min. The mixture was poured in aluminum molds and kept in air ventilated oven at 80°C for the crosslinking reaction. The crosslinked PVA hydrogel was kept in the same condition for 2 days for the complete evaporation of the water. The film was then washed thoroughly with double distilled water and ethanol followed by complete drying. The dried film was ground thoroughly with potassium bromide (KBr) and then pressed to obtain a transparent pellet using a hydraulic press. FTIR spectra were then recorded using Jasco FTIR (Model: Jasco 610).

Pb(II) adsorption experiments

The standard stock solution of Pb(II) (1000 mg/L) was procured from Sigma Aldrich, India and then diluted as per requirement. In typical batch experiments, the hydrogel corresponds to 10 mg MWNTs were swelled in 10 mL standard solution (concentra-



Scheme 1 Methodology adopted for batch adsorption experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion: 1000 µg/L) of Pb(II) in stoppered glass bottles for different time duration (0.5–24 h) at room temperature (25°C ± 1°C). The collected samples were filtered through 0.45 micron filters and immediately determined the concentration of Pb(II) using Atomic Absorption Spectrophotometer (Model: Analytikjena Nova-400) under flame mode. Control experiments in absence of MWCNTs were also carried out to correct any adsorption of metal on PVA surface. The methodology adopted for the adsorption experiments is shown in Scheme 1.

The MWCNT dosage effect on Pb(II) adsorption was carried out by soaking hydrogel contain MWCNT of 0, 1, 2.5, 5, 10, and 20 mg in to 10 mL of Pb solution. The effect of pH on adsorption has been carried out by carrying out the above experiment in the solution containing 1000 µg/L of Pb(II) ion. The initial pH values of the solution were adjusted from 2.3 to 9 using various concentrations of nitric acid and sodium hydroxide. In a similar way, the adsorption isotherm studies was also carried out by repeating the above experiment which having the MWCNT dosage of 5 mg in 10 mL of Pb solution at different contact time varying from 0.5 to 24 h at acidic pH.

Regeneration studies of the hydrogel

The desorption capability of the adsorbent was studied by extracting the metal loaded hydrogel in acidic, basic, and neutral solutions. After giving sufficient time for extraction, the samples were filtered and analyzed.

RESULTS AND DISCUSSION

Characterization of the prepared adsorbent

FTIR spectra of MWCNT, oxidized MWCNT, PVA, and PVA/MWCNT hydrogel were shown in Figure 1. A broad peak around 3290 cm⁻¹ verified the presence of hydroxyl group. Strong signal at 1150 cm⁻¹ was the proof of C–O bond. These two peaks were clear evidences of the successful attachment of PVA on the MWCNTs surface. Corresponding stretches on PVA plot were hydroxyl group from 3000–3600 cm⁻¹, and C–O bonding in the region of 1000–1250 cm⁻¹.

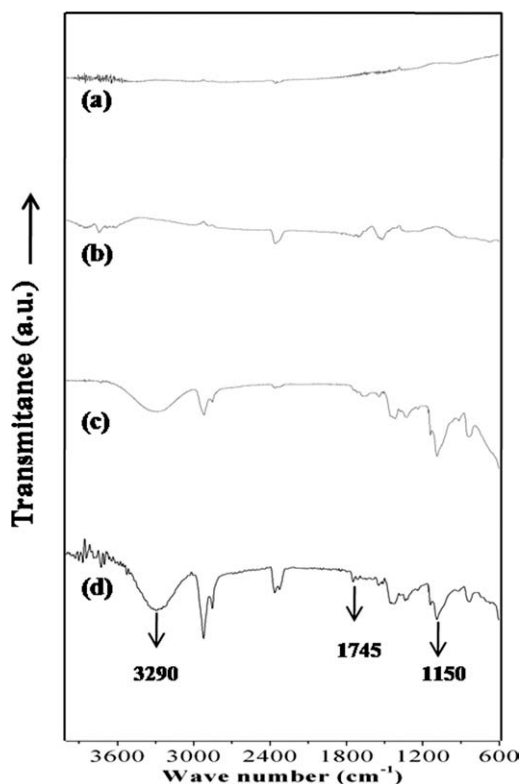


Figure 1 FTIR spectra of (a) MWCNT, (b) Oxidized MWCNT, (c) PVA, and (d) PVA/MWCNT hydrogel.

Also, the peak at around $2850\text{--}2900\text{ cm}^{-1}$ on IR curve of PVA was indication of CH/CH₂ bonding. On the other hand, on the IR curve of MWCNT/PVA hydrogel, some peaks were seen at around $1550\text{--}1745\text{ cm}^{-1}$, which originated from C—C bonding indicating the presence of both MWCNT and PVA.

Figure 2 represents the thermo gravimetric analysis of PVA and the prepared adsorbent containing 0.8 wt% of MWCNT. The thermal stability of the hydrogel was found to be enhanced by the incorpo-

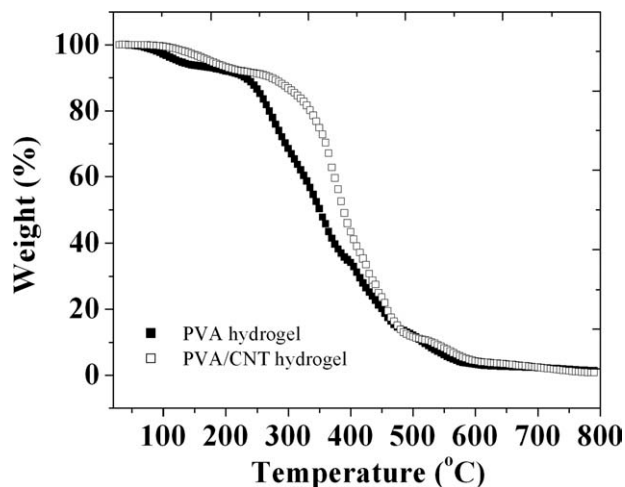


Figure 2 TGA of the PVA hydrogel and the prepared adsorbent

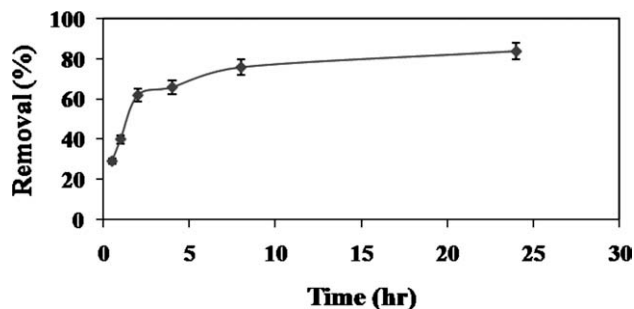


Figure 3 Effect of contact time on the removal of Pb(II) with PVA-based MWCNT hydrogel.

ration of MWCNTs. The prepared adsorbent is stable up to 300°C .

Effect of contact time

The effect of contact time on the removal of the Pb(II) was conducted and the results were shown in Figure 3. The initial concentration of Pb(II) was $1000\text{ }\mu\text{g/L}$, pH of the solution was kept at 3, and the hydrogel containing 2.5 mg of MWCNT was soaked. It is noted that the adsorption of Pb(II) increased with time and then reached equilibrium. The adsorption increased initially, and reached equilibrium value by about 8 h. The final value for the removal was found to be 80%. The contact time for all other studies was kept as 8 h.

Effect of CNT dosage

Table I shows the effect of the MWCNT dosage on the adsorption of Pb(II). The hydrogel itself without the presence of MWCNT shows a minimal amount of Pb(II) adsorption. The adsorption capacities of Pb(II) increase with increasing MWCNT dosage and the contact time was kept as 8 h. The adsorption percentage of Pb(II) was found to be 40, 63, and 83% at a MWCNT dosage of 0, 1, and 2.5 mg, respectively. For the comparison purpose, it was ensured that the volume of the hydrogel containing 0 mg and 1 mg MWCNT kept same. The experimental results revealed that the Pb(II) adsorption increases up to an optimum dosage beyond which the

TABLE I
CNT Dosage Effect on the Pb(II) Adsorption

S. no.	MWCNT dosage (mg/10 mL)	Adsorption (%)
1	0	45
2	1	63
3	2.5	83
4	5	83
5	10	84
6	20	86

Note: The zero CNT dosage corresponds to the hydrogel alone. (Initial concentration $1000\text{ }\mu\text{g/L}$, pH of the solution was kept at 3).

adsorption efficiency does not change.^{21–24} It may be concluded that by increasing the adsorbent dose the adsorption efficiency increases but adsorption density decreases. The decrease in adsorption density can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process; whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in removal efficiency. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial Pb(II) concentration, because for a fixed initial solute concentration, increasing the adsorbent doses provides a greater surface area or adsorption sites.²⁵ This implies that if the nanomaterial is properly dispersed, even a very small amount can absorb more than 80% of the Pb(II) from the solution at an initial concentration of 1000 µg/L.

Effect of pH

The adsorption is aimed to be used in drinking water purification, therefore, adsorption studies were more significant in the neutral pH, but for the comparison purpose we have repeated the experiments in basic and acidic environment also. The adsorbent hydrogel was immersed in the solution with initial concentration of 1000 µg/L of Pb(II) at pH 3, 7, and 9. From the experimental results, it was observed that the adsorption capability of the hydrogel is comparable in acidic (83.5%), neutral (83%), and basic (82%) solutions. It is known that CNTs synthesized may have many defects and are coated with lot of amorphous carbon.^{17,26,27} These defects and amorphous carbon can offer active sites for Pb(II) adsorption on the outer surfaces of CNTs. This may be the reason for the adsorption of Pb(II) within a broad pH value range.

Adsorption isotherm

Single metal ion equilibrium sorption studies were conducted to investigate the maximum metal

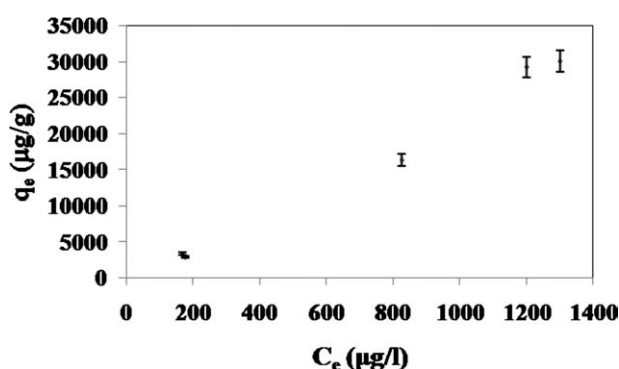


Figure 4 Adsorption isotherms of Pb(II) adsorbed by PVA-based MWCNT hydrogel.

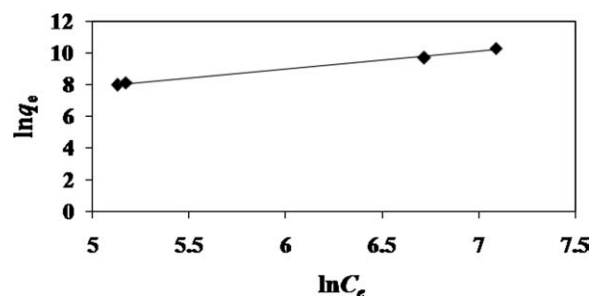


Figure 5 Freundlich isotherm model plot of $\ln(q_e)$ vs. $\ln(C_e)$.

adsorption. It was observed from the Figure 4 that the adsorption of the ions increased with the initial metal ion concentration and reached to a maximum of 3×10^3 µg/g at an equilibrium concentration of 1.2×10^3 ppb.

The equilibrium distribution of Pb(II) between the adsorbent and the solution is important in determining the maximum sorption capacity. Several isotherm models are available to describe the equilibrium sorption distribution in which two models are used to fit the experimental data: Langmuir and Freundlich models.^{28,29} The linear form of Langmuir model is given by

$$C_e/q_e = C_e/Q_{\max} + 1/(Q_{\max} \times K_L) \quad (1)$$

where C_e is the equilibrium metal ion concentration (mg of Pb(II)/L), q_e is Pb(II) concentration on the adsorbent at equilibrium [mg of Pb(II)/g of the dried adsorbent]; Q_{\max} (mg/g) and K_L (L/mg) are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites and a measure of adsorption energy (equilibrium adsorption constant), respectively. These constant are found from the slope and intercept of C_e/q_e vs. C_e linear plot so that $Q_{\max} = 1/\text{slope}$ and $K_L = \text{slope}/\text{intercept}$. In this case, Langmuir adsorption isotherm does not show linearity (Data not included). Hence, we tried with Freundlich model.

The linear form of the Freundlich model is given by:

$$\ln(q_e) = \ln(K_F) + (1/n) \cdot \ln(C_e) \quad (2)$$

where K_F and n are Freundlich constants determined from the slope and intercept of plotting $\ln(q_e)$ vs. $\ln(C_e)$. In this case, the experimental data was not following Langmuir adsorption isotherm. The experimental data fit the Freundlich adsorption isotherm well with a correlation coefficient of 0.995 (Fig. 5).

Regeneration studies

The applicability of adsorbents depends not only on the adsorption capacity but also on the desorption

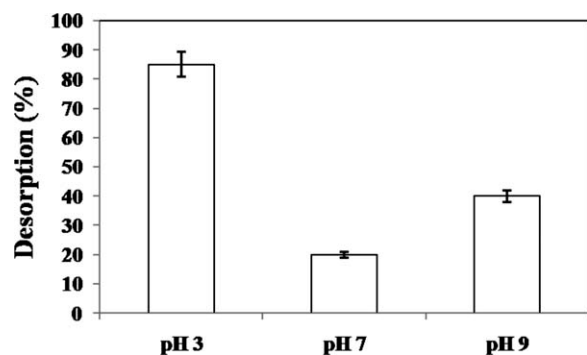


Figure 6 Desorption of Pb(II) ions at different pH

property. For cycle stability of Pb(II) on the adsorbent for recovery, adsorption and desorption of Pb(II) were done at acidic, basic, and neutral solutions. The required amount of hydrogel was soaked in Pb(II) solution at an initial concentration of 1000 $\mu\text{g}/\text{L}$ until equilibrium adsorption attained. The solution was filtered and analyzed for the quantity of the ion adsorbed in the hydrogel. The Pb(II) loaded hydrogel was then dipped in different pH solutions. After giving proper time for desorption, the samples were filtered and analyzed for the metal ion. It was found that 85%, 20%, and 40% metal ion get desorbed in acidic, neutral, and basic solutions, respectively (Fig. 6). Thus, following this manner, it was observed that the material can be regenerated in acidic environment and will be ready for further metal ion removal experiment. This observation leads to a solution for high cost, the important factor currently limiting the use of CNTs in practical environmental protection applications. A similar type of regeneration of the ceria nanoparticle supported CNTs was reported by Peng et al.¹² reported for the removal of arsenate from water. Similarly Wajima³⁰ also reported the regeneration of titanium hydroxide-derived adsorbent for the removal of fluoride ions from industrial waste water.

CONCLUSION

MWCNT-based PVA hydrogel was successfully synthesized and characterized using FTIR. The hydrogel was used as a substrate for the effective dispersion of the CNT and also found as a reusable adsorbent for the Pb(II) removal from contaminated water. It was found that as a result of effective dispersion, a very less amount of CNT (2.5 mg) can remove more than 80% of Pb(II) from the water sample evaluated at an initial concentration of 1000 $\mu\text{g}/\text{L}$. The results found to be comparable in acidic, basic, and neutral conditions. The Langmuir and Freundlich adsorption isotherm models were applied to the equilibrium data at pH 2.9. The equilibrium data fits well with

Freundlich adsorption isotherm than Langmuir isotherm. The adsorbent hydrogel could desorb Pb(II) by controlling the pH of the solution to the acidic region. Thus the adsorbent can be regenerate for further removal process and make the entire process cost effective.

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