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Preparations and characterizations of poly-o-toluidine/Multiwalled Carbon Nanotubes /Sn(IV)tungstate composite ion exchange thin films and its application as Pb(II) selective electrode

Asif Ali Khan*, Shakeeba Shaheen

Abstract

Poly-o-toluidine(POT), Poly-o-toluidine(POT)/multiwalled carbon nanotubes(MWCNTs), Poly-o-toluidine(POT)/multiwalled carbon nanotubes(MWCNTs)/Sn(IV) tungstate (ST) thin films were prepared by solution casting method using polystyrene as a binder. The ion exchange capacity (IEC) of POT/MWCNTs/ST thin film was found 1.05 meqg^{-1}, which is better than the IEC of pure POT (0.7meqg^{-1}) and POT/MWCNTs (0.9 meqg^{-1}). The formation of POT, POT/MWCNTs and POT/MWCNTs/ST ion exchange thin films were characterized by Scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX), Fourier transform infra-red (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). On the basis of results obtained by distribution co-efficient (K_d values) values, Pb(II)selective electrode of POT/MWCNTs/ST thin films was fabricated. A linear response in the concentration range of 1×10^{-9}M-1×10^{-1}M Pb(II) by using POT/MWCNTs/ST thin film electrode was obtained.

Keywords: Ion exchange thin films; MWCNTs thin film; Electroanalytical studies; Pb(II) selective; Thermal stability.

1. Introduction

Composite materials prepared by incorporation of organic polymer into inorganic microporous precipitate are an important and growing field of research. Chemical, thermal and mechanical stabilities of such material encouraged the researcher to explore new possibilities of their applications. The resulting reproducible analytical and electroanalytical applications of these materials suggests a class of new ion exchange materials which were further categorized as granular and fibrous type, conducting and nonconducting, microporous and nanostructured.

Development and growth of carbon nano structured materials have become the focus of research [1-6] in different areas of science and technology. Carbon nanotubes due to small size and high conductivity have been attractive to enhancing the performance of polymer materials. Faiz and coworkers [7-9] studied conducting properties and vapor sensing behavior of composite material prepared by carbon nanotubes. Based on the principle of an interconnected network of conducting tubes, carbon nano net transparent conducting thin films have been receiving significant attention. They offer the possibility of not only a low cost, carbon based transparent conducting materials with exceptional electrical properties, but also, an added flexibility over their transparent conducting oxides counterparts.

A number of organic-inorganic composite ion exchange materials prepared in our laboratory were successfully used in making ion selective electrodes [10-14], few of them [15-17] were Pb(II) selective electrodes in the response range 1×10^{-6}M-1×10^{-1}M. Since chronic exposure comes from lead in paint and tap water, chemical residues in processed foods, and personal care products, detection and determination of lead in traces amount is still a subject of study for researchers related to environmental science or analytical chemistry. In view of above advantages of organic-inorganic composite ion exchange materials and carbon nanotubes, poly-o-toluidine/ multiwalled carbon nanotubes/ Sn(IV) tungstate composite ion exchange thin film is prepared in our present work in order to raise the possibility of its use in many application such as in making ion selective thin films and vapor sensing screen of flexible thin films.

2. Experimental

2.1. Chemicals, reagents and instruments

O-toluidine from E-Merck (India Ltd.), MWCNTs used in this study were purchased from Iljin Nano Tech, Seoul, Korea (diameter ~ 10-20 nm and average length ~ 20 μm). Ammonium persulphate, CTAB (Cetyl trimethylammonium bromide) from CDH (India Ltd.), p-toluenesulfonic acid (pTSA) and tetra hydrofuran (THF) from Qualigens (AR grade), methanol from CDH (India Ltd.), polystyrene were obtained from research design, india and HCl from Merck (India Ltd.) were used as received. Demineralised Water (DMW) was used through the experimental part.

The following instruments were used; FTIR spectrophotometer (Perkin-Elmer, USA, model Spectrum-BX, range 4000-400 nm), Scanning electron microscope (SEM) and Energy dispersive X-ray (EDX) (LEO 435–VF), thermo-gravimetric analysis (TGA) using thermal analyzer-V2.2A DuPont 9900 and Rigaku X-Ray powder diffractometer with Cu anode (Kα λ=1.54186 A°) using a PW, 1148/89 based diffractometer with Cu Kα radiations. A digital potentiometer (Equiptronics EQ 609, India); accuracy 1 mV with a saturated calomel electrode as reference electrode.

2.2. Synthesis of POT, POT/MWCNTs and POT/MWCNTs/ ST composites

In a typical process, CTAB was added to 300 ml of 1M HCl under stirring, which was followed by the addition of monomer o-toluidine. To the above mixture MWCNTs, ultrasonicated in HCl was added and the system was put under vigorous stirring. The solution of oxidant ammonium per sulphate was added later, which changed the colour of the solution from pink to green, indicated the polymerization process of monomer o-toluidine. The whole system was put under vigorous stirring for 24 hours after which the sample was filtered, washed with DMW and later with excess of methanol until the filtrate become colourless. The polymer was later doped with *p*TSA solution, made in EDTA to render it conductive. Pure POT was prepared similarly in the absence of MWCNTs. In the case of POT/ MWCNTs/ST, the inorganic Sn(IV)tungstate (ST) (prepared by mixing 200 ml of 0.1M stannic chloride [prepared in 1M HCl] to 50 ml of 0.1 M sodium tungstate in [prepared in DMW] was added in MWCNTs. The ion exchange capacities (IEC) of these materials were determined by column process (**Table 1**).

2.3. Sorption studies

The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions.

The distribution coefficient (K_d values) of various metal ions on POT/MWCNTs/ST composite were determined by batch method in various solvents system. Various 200 mg sample of the composite exchanger beads (T-10) in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and was kept for

24h with continuous shaking. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005M solution of EDTA**[18]**, While some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{6+}] were determined **(Table 2)**. The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase, or in other words, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and can be mathematically calculated using the formula:

$$K_d = (I - F)/F \times V/M \ (mlg\ ^{1}) \text{..........1}$$

Where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of nano composite cation exchanger (g).

2.4. Preparation and IEC of POT, POT/MWCNTs and POT/ MWCNTs/ST composites ion exchanger thin films

POT, POT/MWCNTs and POT/MWCNTs/ST composite ion-exchanger thin films were prepared 200mg of material with polystyrene by solution casting method. 500 mg polystyrene was dissolved in 50 ml THF at room temperature. Mechanical stirring for at least 24h was applied at room temperature in order to dispersed polystyrene solution. The POT, POT/MWCNTs and POT/MWCNTs/ST composite materials dispersed in polystyrene solution and subsequently casted onto clean glass plates, then kept for 48h at room temperature to allow complete evaporation of THF. The resultant composite ion exchanger thin films were cautiously peeled out of the glass plates and rinsed with DMW on both sides then dried at room temperature. The dried composite ion exchanger thin films were converted into H^+ form through immersion in 1M HNO_3 for 2 days with occasional shaking intermittently replacing the supernatant liquid with fresh 1 M HNO_3 two to three times. The excess HNO_3 was removed after several washings with DMW and finally dried at room temperature.

To evaluate the IEC of POT, POT/MWCNTs and POT/MWCNTs/ST composites ion exchanger thin films where polystyrene used as binder, 1M $NaNO_3$ solution was taken in a beaker and ion exchange thin films in the H^+ form were dipped for 24h. The effluent was then take out and titrated against a standard (0.1M) NaOH solution using phenolphthalein indicator. The conditions of preparation and IEC of composite ion exchange thin films are given in **Table 3.**

2.4.1. Characterization of Composite ion exchange thin films

The XRD data of pure POT, POT/MWCNTs and POT/MWCNTs/ST composites ion exchange thin films were recorded by Bruker D8 diffractometer with CuKa radiation at 1.540 A˚ in the range of $20° \leq 2\theta \leq 80°$ at 40 keV. For Fourier transform infra-red (FTIR) spectroscopic studies of POT, POT/MWCNTs and POT/MWCNTs/ST composites ion exchange thin films, Perkin-Elmer USA, model Spectrum-BX, range 4000-400 nm spectrophotometer was used. A LEO 435-VF scanning electron microscopy (SEM) micrograph and Energy-dispersive X-ray (EDX) studies were also used to obtain composition **(Table 4)** of the thin films. Thermo-gravimetric analysis (TGA) was performed by a Perkin Elmer instrument heating from ~10°C to 1000°C at the rate of 10°C min^{-1} in nitrogen atmosphere with the flow rate of 30 ml min^{-1}.

Physicochemical characterization is also important to understand the performance of thin films. Thus some parameters such as porosity, water content, swelling, and thickness were determined after conditioning of the ion exchange thin films as **Table 5**.

2.4.2. Fabrication of ion-selective thin films electrode

The ion exchange thin films sheet of POT, POT/MWCNTs and POT/MWCNTs/ST composites (0.65 mm thickness) as obtained by the above procedure were cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as reference) towards which the ion exchange thin films are selective and kept in an identical solution of the same ion at room temperature. In case of POT, POT/MWCNTs, POT/MWCNTs/ST composite ion-selective ion exchange thin films electrode, the glass tube was filled with 0.1M $Pb(NO_3)_2$ solution. Saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)	**Internal electrolyte 1×10^{-1}M Pb(II)**	**Ion-exchange thin film**	**Sample Solution 1×10^{-10}–1×10^{-1} M Pb(II)**	**External reference electrode (SCE)**

Following parameters were evaluated to study the characteristics of the electrode such as lower detection limit, electrode response curve, response time and working pH range.

2.4.3. Electrode potential of thin films

The response of the electrode in terms of the electrode potential (at 25±2 ºC), corresponding to the concentration of a series of standard solutions of 0.1M $Pb(NO_3)_2$ (10^{-10} to 10^{-1}M), was determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [19]. Potential measurements of the ion exchange thin films electrode were plotted against the selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

2.4.4 Response time

The response time was measured by recording the EMF of both the electrodes as a function of time when it was immersed in the solution to be studied. The method of determining response time in the present work is being outlined as follows:

The electrode is first dipped in a 1 × 10^{-1}M solution of the ion concerned and immediately shifted to another solution (pH~4) of 1 × 10^{-2}M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second that is, just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 5s. The potentials were then plotted vs. the time. The time during which the potentials attain a constant value represent the response time of the electrode**.**

2.4.5. Selectivity coefficient

The response for the primary ion in the presence of other foreign ions is measured in terms of the Potentiometric selectivity coefficient using mixed solution method [20] **(Table 6)**. The selectivity coefficient was calculated using the equation given below:

$$K_{AB}^{POT} = \frac{a_A}{(a_B)^{ZA/ZB}} \text{................ (4)}$$

Where a_A and a_B are activities of primary and interfering ion of varying concentration of primary ions and fixed concentration of interfering ions and zA and zB are charges on the ions.

3. Result and discussion

POT, POT/MWCNTs and POT/MWCNTs/ST composite ion-exchange materials were prepared by in-situ polymerization. The POT, POT/MWCNTs and POT/MWCNTs/ST composites ion-exchange possessed IEC for Na^+ were 0.95, 1.08 and 1.25meqg^{-1} respectively measured under the similar conditions [**Table 1**]. It is quite evident from the result that the IEC is decreased as MWCNTs added in POT. On addition of Sn(IV)tungstate in the sample POT/MWCNTs, the IEC increased, It is clear from the results that as inorganic group were added into the polymer chain, IEC increases after the formation of composite where more exchangeable sites are available.

In order to explore the potentiality of the material in the separation of metal ions, distribution studies for metal ions were performed in different solvent systems. It was apparent from the data given in **[Table 2]** that the K_d-values can vary with the composition and nature of the contacting solvents. It was observed from the K_d-values in DMW and other solvent systems that Pb(II) is strongly adsorbed where as Cd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Cr^{6+} are comparatively show low adsorption on surface of composite ion exchange material. The high uptake of certain metal ions demonstrates not only the ion-exchange properties but also the adsorption and ion-selective characteristics of the cation-exchanger. The difference in adsorption behavior in different solvents media is largely explained on the basis of differences in the stability constants of the metal-exchanger complexes.

A number of samples of POT, POT/MWCNTs and POT/MWCNTs/ST composite ion-exchange thin films were prepared with 200mg amount of material with fixed amount of binder (500mg polystyrene) and were checked for the mechanical stability, surface uniformity, materials distribution, cracks and thickness, etc. The IEC of POT, POT/MWCNTs and POT/MWCNTs/ST composite ion-exchange thin films for Na^+ were found 0.7, 0.9 and 1.05 meqg^{-1} respectively. Condition of preparation and IEC of composite ion-exchanger thin films given in **Table 3**.

Fig.1 shows the SEM images of POT, POT/MWCNTs, POT/MWCNTs/ST and Pb(II) adsorbed POT/MWCNTs/ST composite ion-exchange thin films at different magnifications. It is observed that the prepared polymeric composite ion-exchange thin films were porous in nature and forms dense thin films. **Fig.1 (d)** shows clear adsorption of Pb(II) in the pores of POT/MWCNTs/ST composite thin film.

The elements present in the POT, POT/MWCNTs, POT/MWCNTs/ST and after adsorption of Pb(II) on POT/MWCNTs/ST composite ion-exchange thin films were C, N, O, Sn, W and P, the percentage composition of these elements in the ion-exchange thin films were verified from **Table 4**.

FTIR spectra of POT, POT/ MWCNTs and POT/ MWCNTs/ST ion exchange thin films are presented in **Fig. 2**. For POT thin film, the band at 1350 cm^{-1} is due to the symmetric deformation of C-H vibration. The band at 958 cm^{-1} can be assigned to the C–N vibration **[12]**. The two bands appearing at 873 cm^{-1} and 812 cm^{-1} were attributed to an out-of-plane C–H vibration due to 1,2,4-substitution in the benzenoid rings, and in-plane C–H vibration of quinoid rings respectively. In the FTIR spectra of POT/MWCNTs composite thin film indicating that *o*-toluidine was polymerized on the surface of MWCNTs and chemical interaction has taken place. The band at 1560 cm^{-1} is shifted from 1350 cm^{-1} and 958 cm^{-1} showing the symmetric deformation of C-H group. In the FTIR spectra of POT/MWCNTs/ST ion exchange thin film, a similar peak at 1560 cm^{-1} as in POT/MWCNTs represents C-H vibration frequency. Assemblies of two peaks at 914 cm^{-1} and 650 cm^{-1} represent Sn-O groups **[12]**.

On the basis of the FTIR and EDX results the schematic representation of the formation of POT, POT/ MWCNTs and POT/ MWCNTs/ST ion exchange thin films are shown in **Scheme 1**.

The TGA curves in **Fig. 3** shows distinct weight losses. In POT polymer thin film the TGA curve shows ~40% weight loss of mass from 100-400°C which may be due to removal of water molecules and later ~25% decomposition of the polymer up to 900ºC was observed. In POT/MWCNTs composite thin film the TGA curve shows ~25% weight loss of mass from 50-250°C due to loss of water molecule and after that a ~20% gradual weight loss was found up to 500°C, another weight loss (~30%) was observed up to 1000°C. The ~20% weight loss in POT/MWCNTs/ST composite ion exchange thin film was noticed between the temperature range 50-200°C after that ~30% gradual decomposition of the thin film was marked up to 500°C then ~40% degradation of POT/MWCNTs/ST composite ion exchange thin film was noted up to 1000ºC. It is quite clear from the results of TGA that POT/MWCNTs composite and POT/MWCNTs/ST ion exchange thin film were thermally more stable than pure polymer i.e. POT.

The X-ray diffraction studies of the POT, POT/MWCNTs and POT/MWCNTs/ST composite ion-exchange thin films (as prepared) were carried out using Rigaku X-Ray powder diffractometer with Cu anode (Kα λ=1.54186A°) in the range of $20° \leq 2\theta \leq 80°$ at 30Kv. **Fig. 4** shows the typical XRD pattern of the thin films at room temperature. It is evident from the XRD pattern that the POT and POT/MWCNTs thin films were formed in the amorphous phase but POT/MWCNTs/ST thin film indicates peaks of semicrystalline phase.

Physicochemical characterizations of ion-exchange thin films were also essential to use it in making ion selective electrode. Thus some properties like swelling, thickness, porosity, water content capacities were determined **[Table 5].** The POT, POT/MWCNTs, POT/MWCNTs/ST composite ion-exchange thin films (thickness 0.015, 0.022 and 0.014 mm respectively) was selected for making ion selective electrode. Thus low order of water content, swelling and porosity with less thickness of these membranes suggests that interstices are negligible and diffusion across the membranes would occur mainly through the exchanger sites.

Sensitivity and selectivity of the ion-selective electrode depend upon the nature of electro-active material. When ion-exchange thin films of such materials were placed between two electrolyte solutions of same nature, but at different concentration of metal (to which membrane is selective) ions, the ion exchange diffusion phenomenon predominates, the ions selective to ion-exchange thin films [Pb(II)] were exchanged by the H^+ present on the surface of the membrane, thus producing an electrical potential difference i.e. membrane potential. The Potentiometric response thin films electrode over a wide concentration ranges 1×10^{-10} M to 1×10^{-1} M is shown in **[Fig. 5]**. The POT electrode shows a linear response in the range of 1×10^{-7} M to 1×10^{-1} M, POT/MWCNTs electrode shows linear response in the range of 1×10^{-8} M to 1×10^{-1} M and POT/MWCNTs/ST electrode shows linear response in the range of 1×10^{-9} M to 1×10^{-1} M. Thus, the working concentration ranges of thin films were found to be 1×10^{-7} M, 1×10^{-8} and 1×10^{-9} to 1×10^{-1} M for Pb(II) in three thin films POT, POT/MWCNTs and POT/MWCNTs/ST respectively.

Another important factor is the response time of the ion-selective electrode. The average response time is defined as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different ion solutions, each having a 10-fold difference in concentration. The response time in contact with 1×10^{-1} M Pb(II)ion solution was determined, and the results are shown in **[Fig. 6]**. It is clear from the figure, that the response time of the POT, POT/MWCNTs and POT/MWCNTs/ST are ~40, ~45 and ~50s respectively.

It is also observed that the thin films could be successfully used up to 14 months without any notable drift in potential during which the potential slope is reproducible within ±1 mV per concentration decade. Whenever a drift in the potential is observed, the membrane is re-equilibrated with 0.1 M $Pb(NO_3)_2$ solutions for 3-4 days.

The selectivity behaviour is obviously one of the important characteristics of the ion-selective electrodes, determining whether reliable measurement in the target sample is possible or not. It was determined by the mixed solution method (MSM). It is evident from **Table 6**, most of the interfering ions showed low values of selectivity coefficient, indicating no interference in the performance of the POT/MWCNTs/ST thin films electrode assembly. Such remarkable selectivity for Pb(II) over other ions reflects the high affinity of the membrane toward the Pb(II) ions.

4. Conclusions

Mechanically and Thermally stable POT, POT/MWCNTs and POT/MWCNTs/ST ion exchange thin films were prepared and characterized by using different instrumental techniques such as SEM, EDX, FTIR, TGA and XRD. These thin films were successfully been used in making ion selective electrode for measuring Pb(II) content in traces amounts. POT/MWCNTs/ST thin film is indicating better working range up to 1×10^{-9} to 1×10^{-1} M for Pb(II).

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Notes and References

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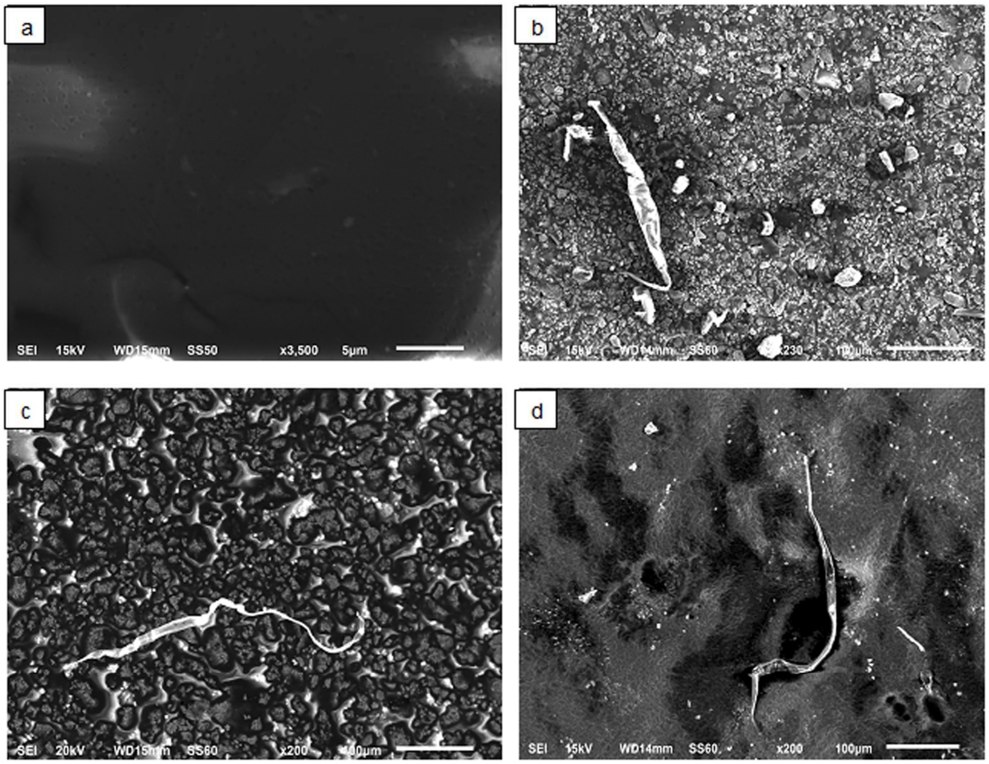


Fig. 1 SEM images of (a)POT, (b)POT/MWCNTs, (c)POT/MWCNTs/ST and (d) Pb(II) adsorbed POT/MWCNTs/ST ion exchange thin films
172x133mm (300 x 300 DPI)

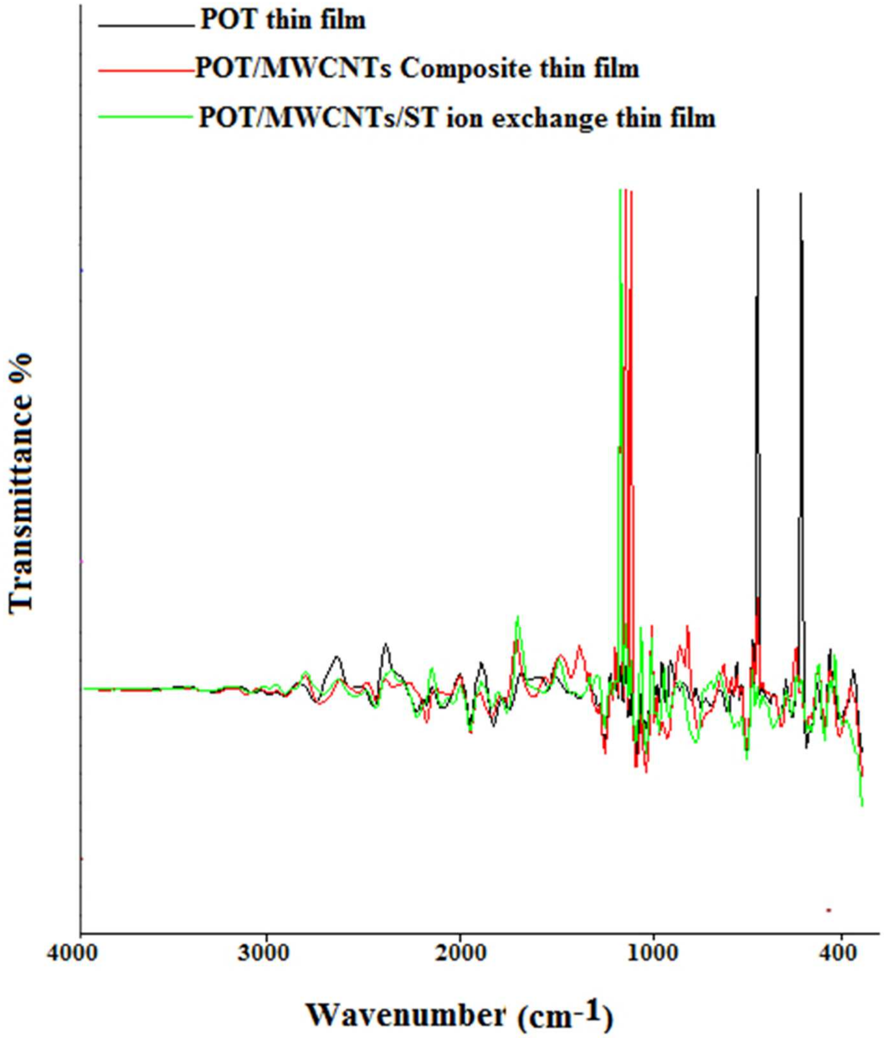


Fig. 2 FTIR Spectra of POT thin film, POT/MWCNTs composite thin film and POT/MWCNTs/ST ion exchange thin films
142x150mm (96 x 96 DPI)

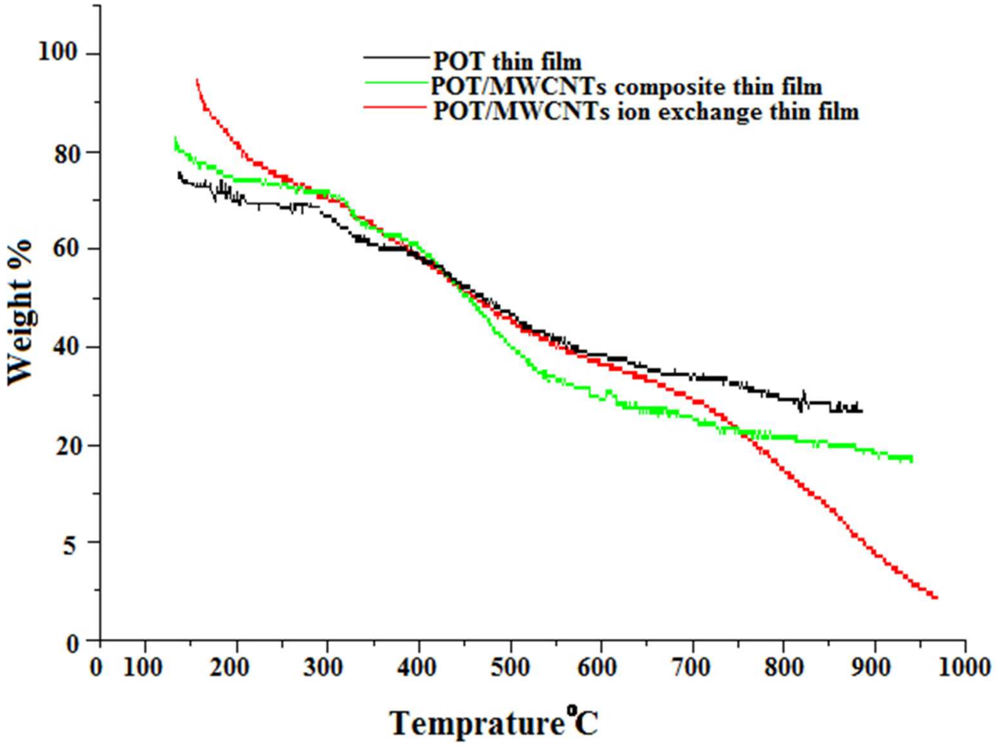


Fig. 3 TGA curves of POT thin film, POT/MWCNTs composite thin film and POT/MWCNTs/ST ion exchange thin films
158x120mm (96 x 96 DPI)

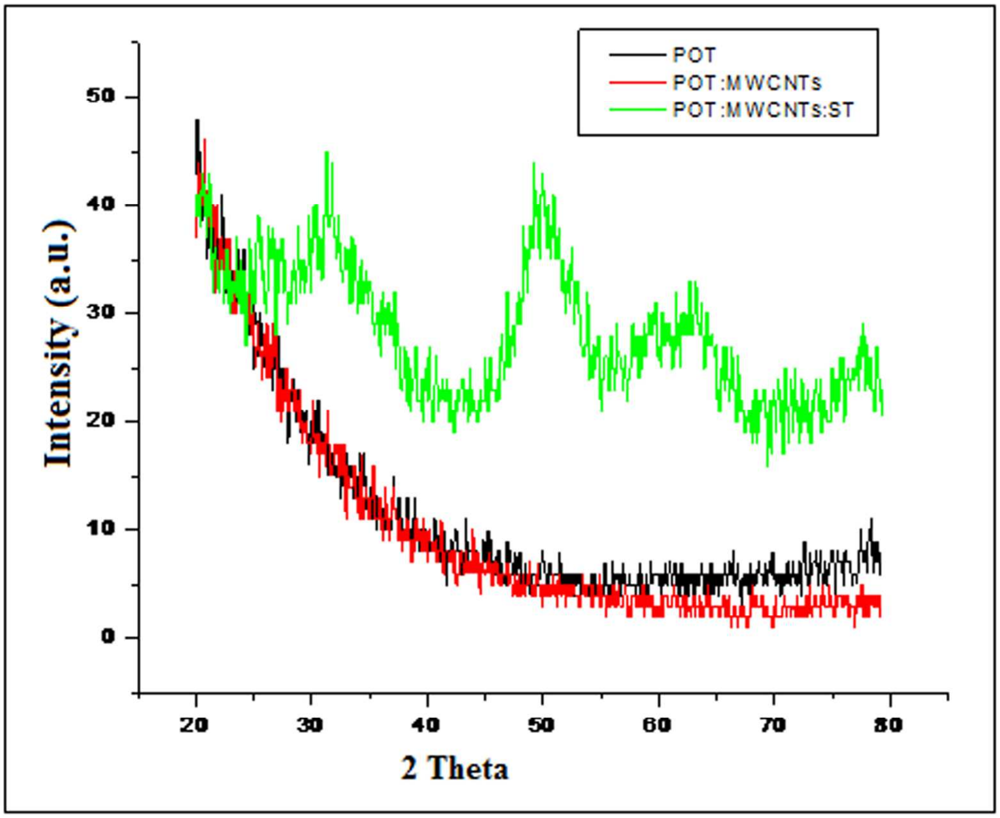


Fig. 4 XRD pattern of POT, POT/MWCNTs and POT/MWCNTs/ST ion exchange thin films
124x102mm (300 x 300 DPI)

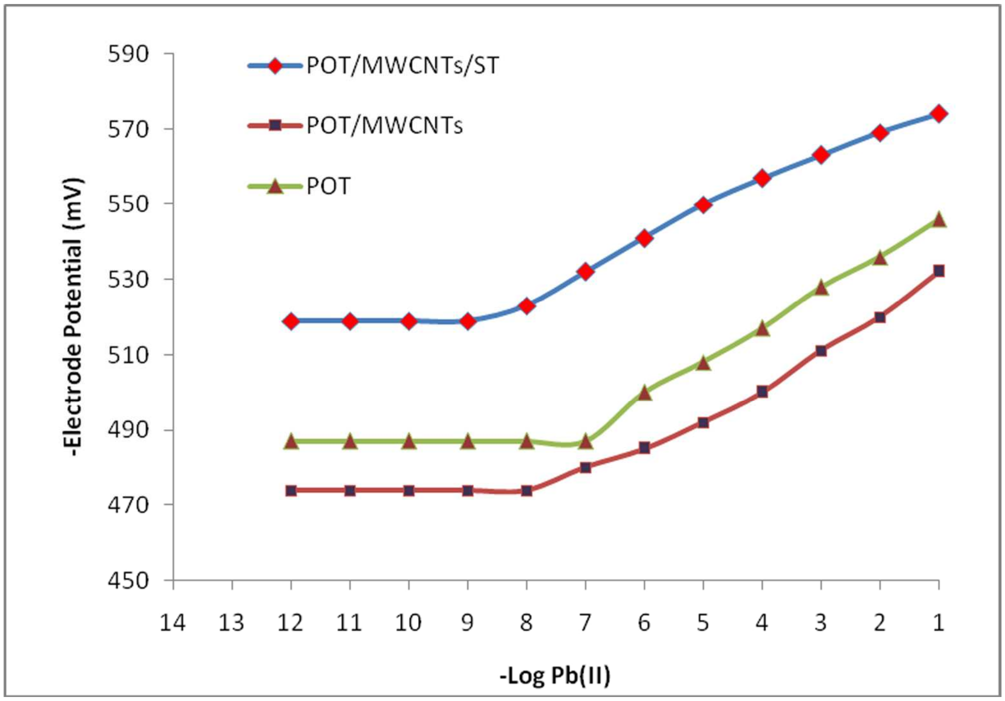


Fig. 5 Calibration curves of POT, POT/MWCNTs and POT/MWCNTs/ST Thin films electrode in aqueous solution of Pb(NO3)2
206x142mm (300 x 300 DPI)

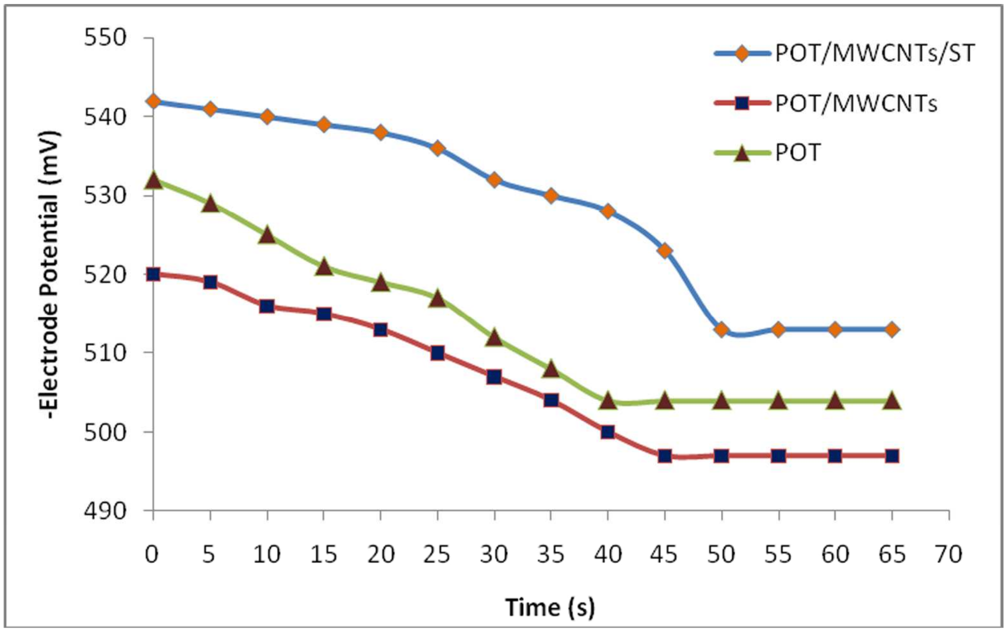
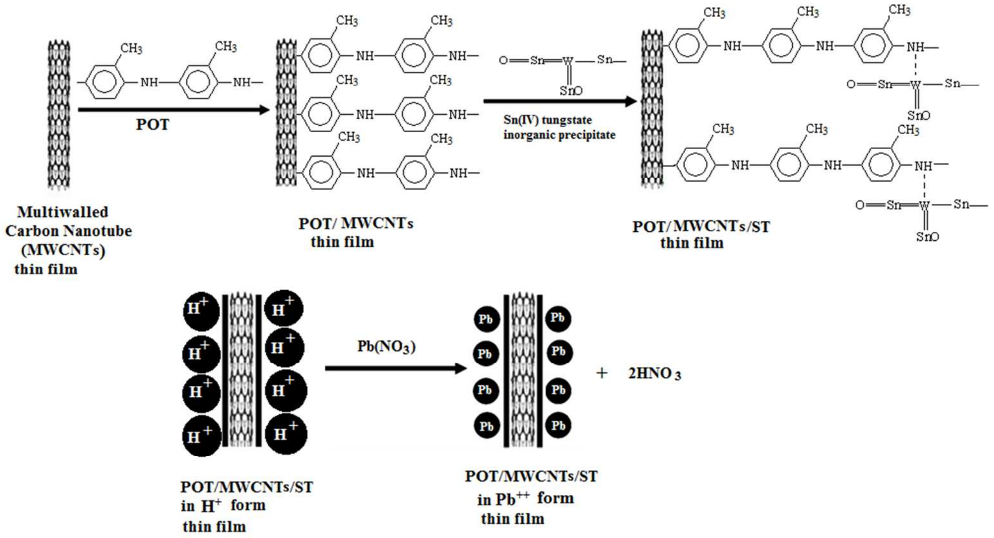


Fig. 6 Time response curves of POT, POT/MWCNTs and POT/MWCNTs/ST Thin films electrodes
199x124mm (300 x 300 DPI)



Scheme 1. The schematic representation of the formation of POT, POT/ MWCNTs and POT/ MWCNTs/ST ion exchange thin films
268x149mm (96 x 96 DPI)

Table 1. Conditions of preparation and the IEC of POT, POT/MWCNTs and POT/MWCNTs/ ST composites

S. No	**o-toluidine (mL)**	**Oxidant[*] (g)**	**MWCNTs (g)**	**CTAB (g)**	***p*TSA[**]**	**I.E.C. (meqg^{-1})**
POT	5	5.4	0.0	17	8.8	0.95
POT/MWCNTs	5	5.4	0.5	17	8.8	1.08
POT/ MWCNTs/ST	5	5.4	0.5	17	8.8	1.25

[*] Oxidant solution was prepared by dissolving $(NH_4)_2S_2O_8$in 200 mL of 1M HCl

[**] *p*TSA solution was made by dissolving *p*TSA in 500 mL of EDTA

Table 2. K_d values of some metal ions on POT/MWCNTs/ST composite in different solvent systems

Metal ions / Solvents	**DMW**	**0.1M HNO_3**	**0.1M H_2SO_4**	**0.1M HCl**	**10% C_2H_5OH**
Ni^{2+}	41	86	40	71	55
Pb^{2+}	**259**	**550**	**417**	**537**	**223**
Hg^{2+}	61	85	105	189	110
Cd^{2+}	184	145	17	32	74
Cr^{6+}	31	TA	76	TA	TA
Cu^{2+}	70	29	60	102	62

TA= total

Table 3. Condition of preparation and IEC of POT, POT/MWCNTs and POT/MWCNTs/ST ion exchange thin films

S. No.	**composites (gm)**	**Binder**		**IEC of thin films ($Meqg^{-1}$)**
		Polystyrene (gm)	**THF (ml)**	
POT	0.2	0.5	50	0.7
POT/MWCNTs	0.2	0.5	50	0.9
POT/MWCNTs/ST	0.2	0.5	50	1.05

Table 4. Percent composition of POT, POT/MWCNTs and POT/MWCNTs/ST composite thin films

S. No.	**Element**	**Percentage (%)**			
		POT	**POT/MWCNTs**	**POT/MWCNTs/ST**	**Pb(II) absorbed POT/MWCNTs/ST Thin film**
1	**C**	94.21	64.54	82.93	56.16
2	**N**	2.06	8.14	0.44	18.98
3	**O**	3.74	27.32	6.87	19.75
4	**Sn**	-	-	4.80	1.42
5	**W**	-	-	4.96	1.87
6	**Pb**	-	-	-	1.82

Table 5. Physicochemical Characterizations of POT, POT/MWCNTs and POT/MWCNTs/ST ion exchange thin films

S. No.	**Thickness of the thin films (mm)**	**Porosity**	**Water content as % weight of wet thin films**	**Swelling**
POT	0.015	7.4×10^{-3}	1.00×10^{-1}	No swelling
POT/MWCNTs	0.022	1.1×10^{-2}	2.24×10^{-2}	No swelling
POT/MWCNTs/ST	0.014	1.16×10^{-1}	1.3×10^{-1}	No swelling

Table 6. The selectivity coefficient of various interfering ions for Pb(II) selective POT/MWCNTs/ ST composite thin films

Interfering ions (M^{n+})	**Selectivity coefficients (K_{MSM})**
Pb^{2+}	1
Ni^{2+}	1.7×10^{-2}
Cu^{2+}	2.1×10^{-2}
Cr^{6+}	0.9×10^{-3}
Hg^{2+}	4.0×10^{-2}
Cd^{2+}	3.5×10^{-2}

Graphical abstract: