

# In situ Development of nanosized Poly-o-Toluidine (PoT) for sensing volatile Organic compounds

Sangita Satpute<sup>1</sup>, Lalasaheb Kashid<sup>2</sup>, Milind Kulkarni<sup>3</sup>

Department of Chemistry, Vidhya Pratishthan's College, Baramati, Pune, Maharashtra, India<sup>1,2</sup>

Nanocomposite Laboratory, Centre for Materials for Electronics Technology (C-MET), Pune<sup>3</sup>

sangitathoratvp@gmail.com<sup>1</sup>, lmkashid@gmail.com<sup>2</sup>, milindcmet@gmail.com<sup>3</sup>

**Abstract:** Nanosized Poly O toluidine (PoT) were synthesised by in situ oxidative polymerization of monomer o-Toluidine by means of Interfacial Polymerization, leads to the formation of homogenous porous and hollow Fabrililar polymer having approximate diameter 150 nm. Electronic, FT – IR spectra, XRD of resulting nanocomposite shows all characteristic peaks and confirms the presence of conducting emeraldine salt (ES) phase of the polymer. Formed nanosized poly o-toluidine was successfully utilized for sensing volatile organic compounds.

**Keywords:** Interfacial polymerization, Nanosized, POT, sensor, Volatile Organic compounds (VOCs)

## I. INTRODUCTION

With rapid industrial development and population explosion there are two major problems i.e. Depilation of natural energy sources and environmental pollution. Due to increased level of environmental dangerous gases SO<sub>2</sub>, CO<sub>2</sub>, (NO)<sub>x</sub>, variety of toxic organic compounds like chloroform, CCl<sub>4</sub> Benzene, Toluene, sensing and monitoring of different process parameters such as temperature, toxic chemicals, humidity, pH, pressure etc. has been the subject of great interest There is now increased need for low cost, low power, highly sensitive and selective sensors. Future progress in the field of microelectronics, energy storage, sensors and biosensors is concerned with new multifunctional nanostructured materials. Conducting electro active organic polymers are relatively new materials studied from last two decades in sensing applications[1-5] due to interesting electrical, optical and mechanical properties they can be used in a position where inorganic materials are not suitable. The reversible doped and dedoped chemistry of conducting polymers and their wide range of conductivity make them very useful in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants). Therefore, they are sensitive to wide range of volatile organic vapours, humidity, PH etc. selective sensing of various organic vapours such as NH<sub>3</sub>, alcohol, chloroform, etc. shows good potential in remediation of environmental pollution.

Poly O-Toluidine is one of substituted derivative of polyaniline in which –CH<sub>3</sub> is introduced at ortho position of benzenoid ring of polyaniline. MacDiarmid and co-workers suggested that substitution of methyl group at ortho position, increases steric interactions between benzenoid rings along the polymer chains, resulting decrease in the extent of conjugation[6]. Poly O-toluidine shows faster reversibility between oxidized and reduced form therefore chosen as an active conductive polymer along with polyaniline[7,8]. In the present work we have tested the Poly O-Toluidine for sensing Volatile organic compounds such as Benzene, Toluene and chloroform.

## II. MATERIAL AND METHOD

### 2.1 Synthesis of Nanosized poly o- Toluidine

Nano sized POT were synthesized by unstirred interfacial polymerization. In a typical polymerization process, the appropriate amount (0.553 M) of the monomer (O-Toluidine) was dissolved in the organic solvent (chloroform) to form the organic phase. The aqueous phase consists of the oxidizing agent, ammonium per sulphate 1M dissolved in double distilled water together with *p-Toluene sulfonic acid* (PTSA) (1.33 M) as a protonic acid. The monomer to oxidizing agent ratio was kept as 1:1.5. After complete addition of the oxidizing agent (aqueous phase) to the reaction mixture (organic phase) slowly, the two phases are formed and the polymerization is observed to be initiated at the boundary or

at the junction of the two phases. **Figure 1** show different steps involved during the polymerization process. After completion of the reaction the polymer was separated and washed with distilled and then dried for consecutive characterizations and applications.



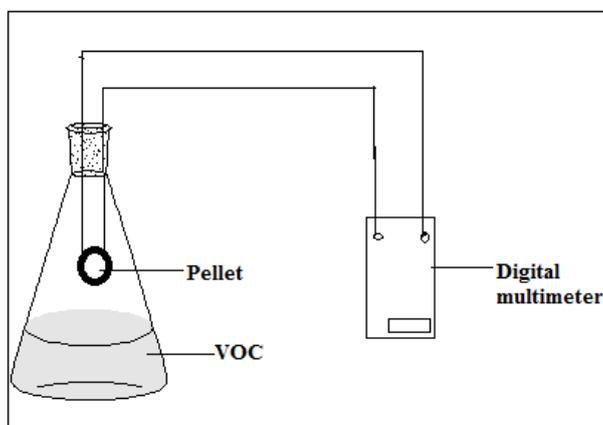
**Figure 1:** Various steps involved during the interfacial polymerization

## 2.2 Structural Characterizations

To study the morphology, structure and stability of the formed material, it was characterized by UV-visible, FT-IR spectroscopy, SEM, X-ray diffraction and TGA.

## 2.3 Sensor Study

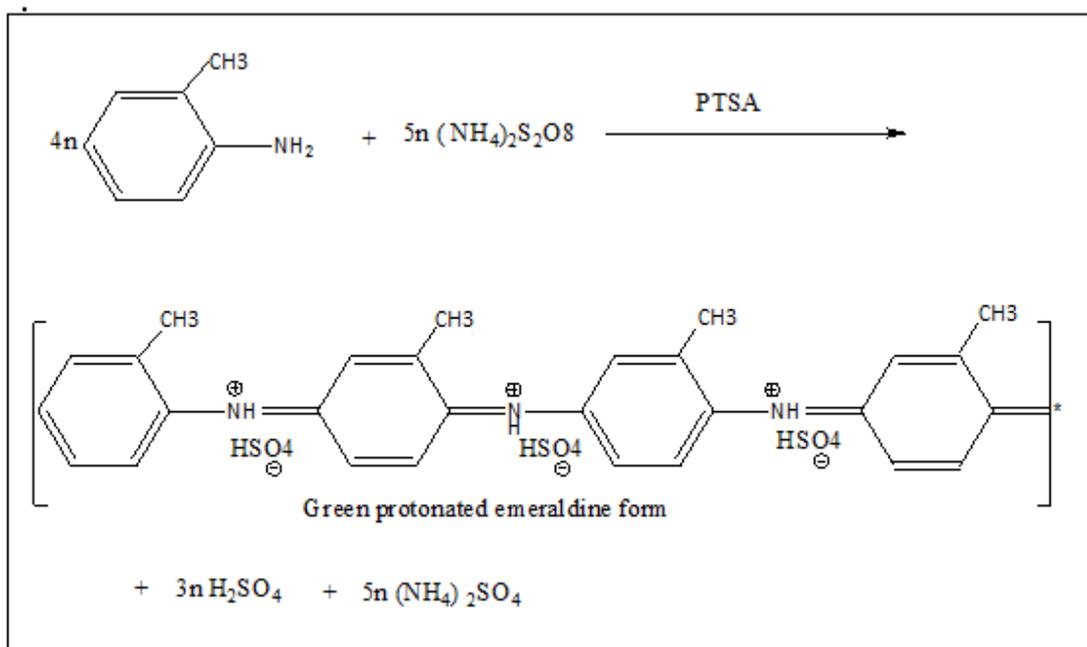
The synthesized Poly O-Toluidine were obtained in the pellet form were used as a sensors. Sensing performance was tested by exposing the pellet sensor to VOC vapours in a close container. The dc electric resistance was measured by simple two probe technique. The container was filled with 50 ml volatile organic compounds and then tightly closed for 24 hrs. So the container was saturated with volatile organic compound vapours and then pellet was hanging in the container about 2cm above the analyte surface. Very thin copper wires acts as a contact leads are fixed 1cm apart from each other on one of the surface using curative silver paste. Resistance was measured as a function of time on a digital millimetre. Experimental set-up is shown in fig. 2. Resistance data was collected by exposing the sensor to VOC vapours and to atmosphere for 5minutes each.



**Figure 2:** Experimental set-up of VOC sensor Testing

### III. RESULT AND DISCUSSIONS

Nanosized poly o-toluidine (POT) was synthesized by chemical oxidative polymerization of O-Toluidine using ammonium per Sulphate as an oxidizing agent in aqueous acidic medium as shown in scheme1. Interfacial polymerization involves the reaction of monomer dissolved in an organic phase with an oxidizing agent dissolved in an aqueous phase at the interface between the two non-miscible phases. The initially formed polymer molecules have affinity towards the water and get diffused in water phase from the boundary, thereby second front of the monomer molecules come in contact with the oxidizing agent and acid and the polymerization proceeds until all the monomer molecules present in organic phase get reacted. So this controlled approach leads to formation of nanosized Fabrialar poly O-Toluidine.

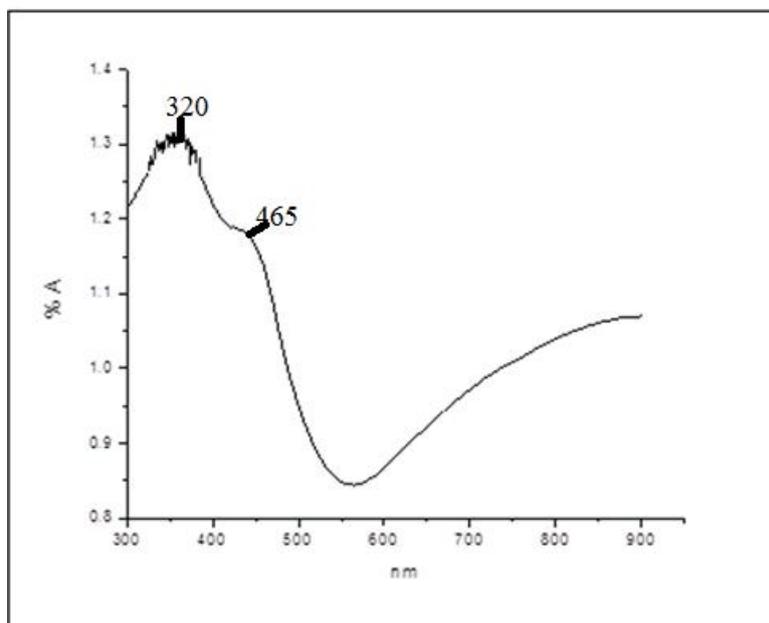


**Scheme 1:** Polymerization of O-Toluidine using Ammonium per Sulphate

### 3.1 Characterization

#### A. UV-VIS Spectra

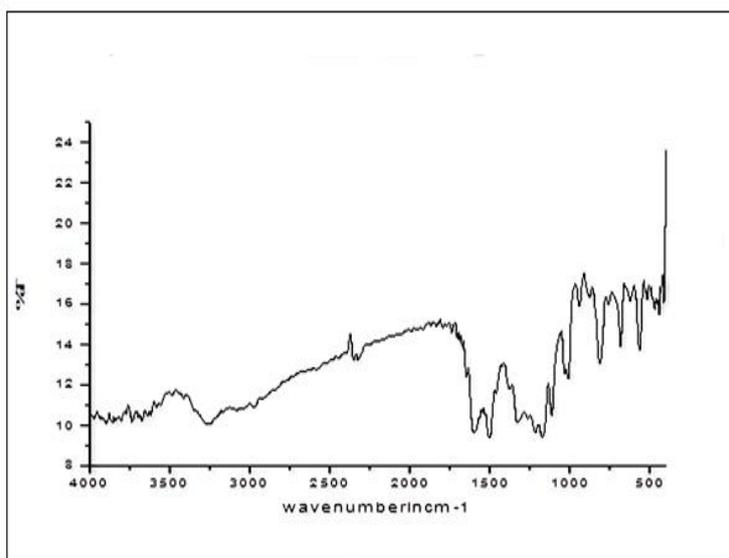
To investigate the oxidation and doping state of the polymer backbone, the optical absorption spectra of the poly O-Toluidine doped with p-TSA was recorded in aqueous solution in the range of 300-1000 nm using Perkin Elmer Lambda -25 double beam spectrophotometer. Electronic spectra of POT was presented in fig.3 It was observed that the spectral pattern of POT is very similar to polyaniline. The spectra exhibits sharp peak at 320 nm which corresponds to the  $\pi$ - $\pi^*$  transition of the benzenoid rings, while the shoulder at 420 nm is attributed to the localized polarons which is the characteristic of the protonated poly o-Toluidine. The peak at 450 nm is attributed to the excitation of Quinone diimine structure (N=Q=N, Q: quinoid) While, the increasing absorption at higher wavelength (~ 800) nm confirms the presence of conducting emeraldine salt (ES) phase of the polymer. A slight hypsochromic shift was observed in the peak positions of POT. Due to increasing the steric interactions among aromatic rings in the polymer chains which decreases extent of conjugation [9].



**Figure 3:** Electronic spectra of POT

### B. FT- IR Spectra

Formation of copolymers, presence of a functional group on the polymer backbone or change in the protonation-deprotonation equilibrium of emeraldine can be deduced from the presence of corresponding bands in the FTIR spectra. The FT-IR spectrum of the emeraldine salt form of POT is given in fig.4 shows all characteristics peaks of POT which are in good agreement with reported literature.



**Figure 4:** FT-IR spectra of POT

The broad and intense peak at  $3300\text{ cm}^{-1}$  has been assigned to secondary  $\text{-NH}$  stretching and vibrational peak at  $1300\text{ cm}^{-1}$  due to C-N stretching vibration clearly shows the presence of ammine and imine units. The less significant peak at  $3000\text{ cm}^{-1}$  is attributed to  $\text{-C-H}$  stretching while small peak at  $2900\text{ cm}^{-1}$  is specifically indicates the C-H stretching of substituted  $\text{-CH}_3$  group. The presence of two intense absorption peaks in the region of  $1600\text{-}1650\text{ cm}^{-1}$  is because of C=C stretching vibration of benzenoid and quinoid rings indicates the polymer backbone is made up of

benzenoid and quinoid rings The peak at  $1150\text{ cm}^{-1}$  is due to  $\text{NH}^+\bullet$  and at  $1000\text{ cm}^{-1}$  for S-O stretching of  $-\text{SO}_3\text{H}$  group confirms the doping state of polymer. Appearance of a significant peak at  $820\text{ cm}^{-1}$  convinced the Para coupling of phenyl rings of O-toluidine during the polymerization [10]. The peak at  $630\text{ cm}^{-1}$  has been designated for-C-H out of bending vibration.

### C. X-Ray diffraction studies (XRD)

Partial crystalline nature of poly O-Toluidine was confirmed from the xrd pattern spectacles in fig. 5The broad characteristic peaks appears at  $19.30^\circ$  and  $25.18^\circ$  represents the (020) and (200) planes of poly o- toluidine. While very sharp peaks at  $2\Theta = 9.22$  and  $16$  represent the polymeric material was nanosized (11) .As compared to polyaniline the peak positions shifted to lower degrees indicating the increasing interplane distance(12)and decreasing the extant of conjugation due to torsional strain caused by substituted methyl group.

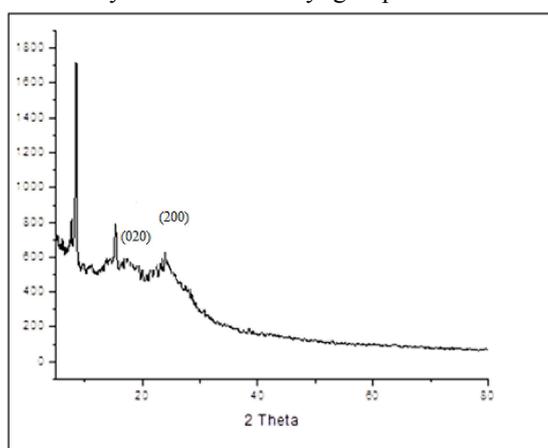


Figure 5: XRD pattern of POT

### D. Thermo- gravimetric Analysis

Poly O-Toluidine shows three step degradation pattern in the temperature range from 25 to  $800^\circ\text{C}$  similar to polyaniline as shown in Fig.6 In the first step there is about 5% weight loss from room temperature to  $110^\circ\text{C}$ . is definitely due to removal of free water from polymer matrix .In the second step start from  $110^\circ\text{C}$  to about  $300^\circ\text{C}$  there is a very few % weight loss by virtue of eliminating the dopant ions as well as bound water from polymer chains. In the third stage from  $300^\circ\text{C}$  onwards polymer starts to degrade and decompose after elimination of dopant ions. There was very great weight loss in case of pot in the third stage indicating more torsional strain because of  $-\text{CH}_3$  side chain decreases its stability, There is a maximum weight loss  $300\text{-}400^\circ\text{C}$  corresponds to oxidative combustion of POT. Above  $500^\circ\text{C}$  weight loss is accounted for complete degradation of quinoid ring structure.( 13-14 )

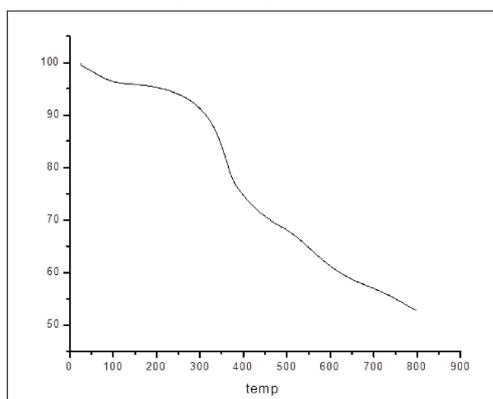
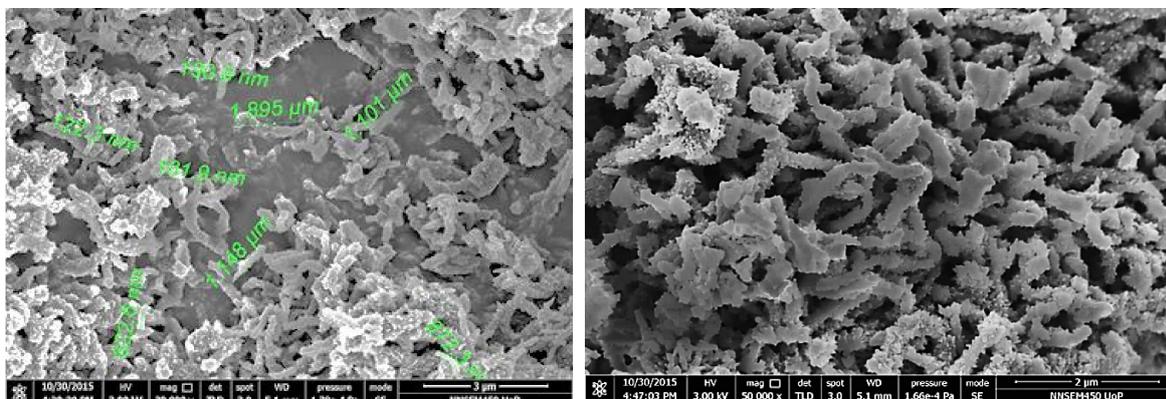


Figure 6: Thermogram of POT

**E. Morphological Studies (FE-SEM analysis)**

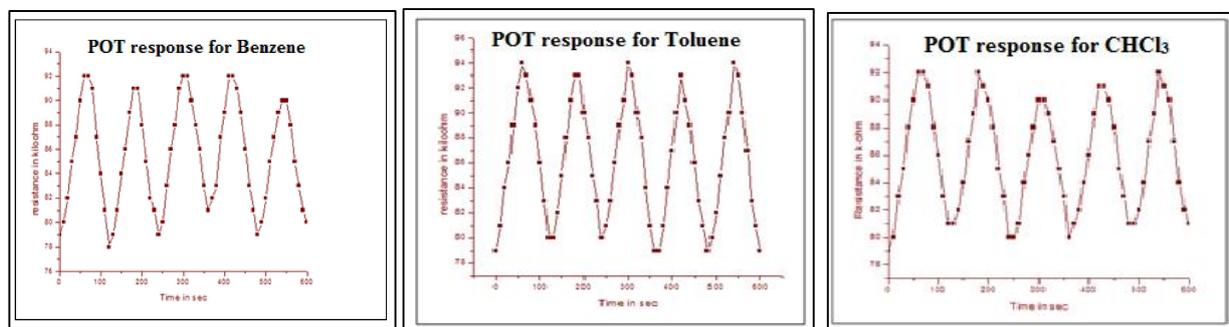


**Figure 7:** FE-SEM micrographs of poly O-Toluidine.

To reveal the Morphological features of formed polymeric material scanning electron microscopy was used. fig.7 SEM micrographs illustrate the surface morphology of formed polymeric material. Unstirred interfacial polymerization offers homogenous porous and hollow fibrillar morphology having approximate diameter 150 nm.

**3.2 Sensor Study**

From the figure it was observed that POT sensor shows change in resistance when expose to saturated vapours of volatile organic compounds and air. There is a positive response in vapours which changes negative in air. The sensor detect the change in resistivity caused by weak physical interactions adsorption or absorption of volatile organic vapours onto polymer chains. There are different types of response mechanisms for detection of organic vapours by polymeric material. These includes weak physical interactions, polymer chain Conformational change, swelling of polymers, change in the doping level and electrostatic and dipole interactions [15-18] It has been reported that all these vapours diffused into the polymer chains causes increased in interchain distance which makes difficulty in hopping of electrons over the polymer matrix results in increasing the resistance that is clearly observed in the response given by VOC in **Fig 8**. Structural features of VOCs play an important role in deciding the extent of diffusion of VOC into polymer matrix. Larger size aromatic hydrocarbon part of Benzene, Toluene makes their adsorption restricted into polymer chain. While small size, moderate polar nature of chloroform increases its Vander-waal interactions with polymer matrix .Because of that it diffuses deeply into polymer chains which make its desorption from polymer matrix difficult. Conductivity of chloroform does not reach to original state.



**Figure 8:** Sensing response of POT given to Volatile organic compounds (VOCs)

**IV. CONCLUSION**

Nanosized poly O Toluidine were successfully synthesised by rapid but controlled Interfacial polymerization. This controlled technique offers fibrillar morphology due to controlled availability of the monomer at the interphase. UV –

VIS and FT-IR spectroscopic analysis confirms the doping state of the polymer. Partial crystalline nature of poly O-Toluidine was confirmed from the XRD pattern and is supported by TGA.FE-SEM analysis reveals homogenous porous and hollow Fabrililar morphology having approximate diameter 150 nm. The synthesised polymer has shown better performance for sensing volatile organic compounds

#### ACKNOWLEDGMENT

MVK would like to thank DeitY, New Delhi for financial assistance and Director, C-MET, Pune for constant encouragement. SMT and LMK would like to thank Department, VP College, Baramati for providing lab facilities.

#### REFERENCES

- [1]. HuaBai and Gaoquan Shi 'Review Gas Sensors Based on Conducting Polymers Sensors' 2007, 267-307
- [2]. W. Li, N. D. Hoa, Y. Cho, D. Kim and J. S. Kim, Sens.Actuators, B, 2009, 143, 132–138.2.
- [3]. P. C. Iekha, M. Balaji, S. Subramanian and D. P. Padiyan, Curr. Appl. Phys., 2010, 10, 457–467.
- [4]. Q. Fan, Z. Qin, T. Villmow, J. Pionteck, P. P'otschke, Y. Wu, B. Voit and M. Zhu, Sens. Actuators, B, 2011, 156, 63–70.
- [5]. O. Y. Posudievsky, N. V. Konoschuk, A. L. Kukla, A. S. Pavluchenko, Y. M. Shirshov and V. D. Pokhodenko, Sens. Actuators, B, 2011, 151, 351–359.
- [6]. Y. Wei, W.W. Focke, GE. Wnek, A. Ray and A.G. MacDiarmid, J.Phys. Chem., 93 (1989) 495.
- [7]. KiranKumari, Vazid Ali, Gita Rani1, Sushil Kumar, G. B. V. S. Lakshmi, M. Zulfequar 'DC Conductivity and Spectroscopic Characterization of Poly (o-toluidine) Doped with Binary Dopant ZrOCl<sub>2</sub>/AgI' Materials Sciences and Application, 2011, 2, 1049-1057
- [8]. Kareema. M. Ziadana, Hussein. F. Husseinb, and K.I.Ajeel, 'Study of the electrical characteristics of poly( o-toluidine) and application in solar cell Energy Procedia' 18 (2012) 157 – 164
- [9]. Meixiang Wan, Jiping Yang 'Studies on the structure and electrical properties of poly (o-toluidine).' Synthetic Metals 73 (1995) 201-204
- [10]. Bagheri A, Nateghi M. and Massoumi A.: Synth. Met., 1998, 85
- [11]. Üçhöyük, Canan, Karakışla, Meral Saçak, Mehmet' Preparation of poly(o-toluidine)/polyacrylonitrile composite fibres using CrO<sub>3</sub>' Indian journal of Fibre and Textile research 37, (2012) ,120-126
- [12]. Y.B. Moon, Y. Cao, P. Smith and A.J. Heeger, Pofym. Commun., 30(1989) 196
- [13]. Kareema. M. Ziadana, Hussein. F. Husseinb, and K.I.Ajeel Study of the electrical characteristics of poly (o-toluidine) and application in solar cell Energy Procedia 18 (2012) 157 – 164
- [14]. Salma Bilala, Shehna Farooqa, Anwar-ul-Haq Ali Shahb, Rudolf Holzec, 'Improved solubility, conductivity, thermal stability and corrosion protection properties of poly(o-toluidine) synthesized via chemical polymerization' Synthetic Metals 197 (2014) 144–153
- [15]. W. Li, N. D. Hoa, Y. Cho, D. Kim and J. S. Kim, Sens.Actuators, B, 2009, 143, 132–138.
- [16]. M. M. Ayad, G. El-Hefnawey and N. L. Torad, J. Hazard.Mater., 2009, 168, 85–88.
- [17]. E. Segal, R. Tchoudakov, M. Narkis, A. Siegmann and Y. Wei, Sens. Actuators, B, 2005, 104, 140–150.
- [18]. S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, Nano Lett., 2004, 4, 491–496.