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# Synthesis and characterization of polyaniline nanocomposite by using several types of surfactants in aqueous media

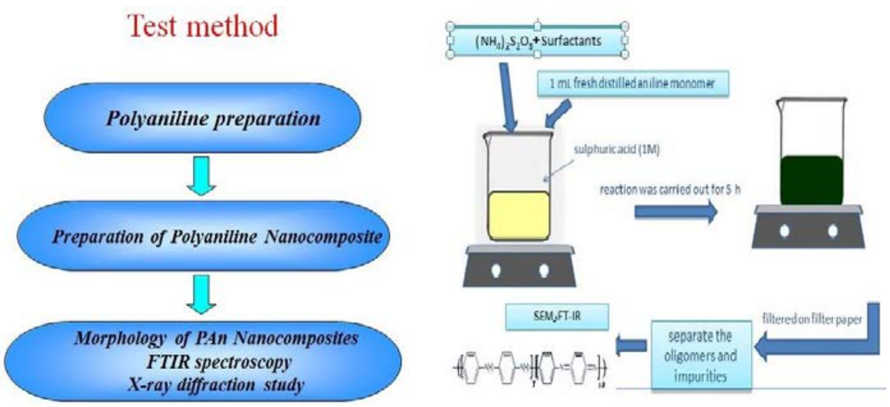
**Milad Hallajiqomi, Mohsen Mehdipourghazi*, Farshad Varaminian**

*Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, 35131-19111, Semnan, Iran*

## HIGHLIGHTS

- Polyaniline (PANI) nanocomposite has been successfully prepared in aqueous media.
- The structural and thermal properties of the nanocomposite were studied.
- The XRD presented partly crystalline structure of PANI in the PANI nanocomposite.
- The physicochemical properties of the solution affected the properties of the products.
- Surfactant disperses uniformly in polyaniline matrix and leads to grain size about 74 nm.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Polyaniline (PANI) nanocomposite has been successfully prepared in aqueous media by the chemical polymerization of aniline with ammonium peroxydisulphate as an initiator in the presence of a steric stabilizer such as sodium dodecylbenzenesulfonate (DBSNa), Poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG) and hydroxypropylcellulose (HPC). The chemical structure, morphology, thermal stability and thermal degradation of the synthesized PANI nanocomposite were studied by different techniques such as fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD) and four-probe. The results revealed that surfactant dispersed uniformly in polyanilin matrix and made a nanocomposite with average crystallite size about 74 nm.

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* *Corresponding author. Tel.: +98 2333383922; fax: +98 2333654284*
*E-mail address: mohsenmehdipour@semnan.ac.ir*

## 1. Introduction

Polyaniline (PANI) is difficult to dissolve and melt, especially in their doping state. It is possible to improve the processability of PANI incorporating functionalized organic acids doping like p-toluenesulfonic and camphor sulfonic acids. The problem in this approach is the interaction between external dopants and the conducting polymer backbone. The structure modification of ring substitution is one of main methods to improve polyaniline solubility. Unfortunately, introduction of ring-substituted groups is detrimental to polymer's conductivity. In order to lessen the effect of substituted groups on polymer electric property, many people pay more and more attention on copolymerization of aniline with other substituted aniline [1–6], such as o-toluidine [4], o-ethyloxyaniline [5], o-aminobenzoic acid [6], and so on.

Polyaniline which is soluble in common organic solvents have been synthesized by using organic acids of large molecular size or graft polymerization with poly (aminostyrene) [7]. Particle size and conductivity can be decreased by increasing the concentration of stabilizer [8, 9]. These are related to the mass of insulating stabilizer adsorbed.

The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable, either by a solution technique or by melt processing methods [10, 11]. Improvement of these material properties can be achieved by forming copolymers, composites, or blends with commercially available polymers or with inorganic materials which offer better mechanical and optical properties, stability and process ability [12-18].

Conducting polymers have various applications such as rechargeable batteries [19], heavy metals separation [20-22], antistatic coatings [23], biomedical applications [24], and so forth.

## 2. Experimental

### 2.1.Instrumentation

A magnetic mixer (Helmer model MK20, Germany), digital scale (Helmer model FR 200, Germany), scanning electron microscope (HITACHI Model S-3000H), fourier-transform infrared spectrometer (Shimadzu model 4100), were employed to characterize the synthesized nanocomposite. The pH of the solutions was measured by a PHS-3BW model pH-meter (Bell, Italy). X-ray diffract meter (X-ray XPERT-PRO) was employed to characterize the synthesized nanocomposite.

### 2.2. Reagents and standard solutions

Materials used in this work were aniline (extra pure >99%, d =1.02 g/cm$^3$), ammonium peroxy disulfate ($(NH_4)_2S_2O_8$), hydroxypropyl cellulose (HPC, Mw =10$^6$ ) were from Aldrich. Sodium dodecylbenzenesulfonate (DBSNa) was from Loba chemie. Poly (vinyl pyrrolidone) (PVP, Mw=25000), poly (vinyl alcohol) (PVA, Mw =72000), poly (ethylene glycol) (PEG, Mw =35000) from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water, sulfuric acid and ethyl acetate were used throughout this work. Aniline monomer was purified by simple distillation.

### 2.3. Polyaniline preparation

For preparation of polyaniline nanocomposite, 1 g ($(NH_4)_2S_2O_8$) and 0.4 g of DBSNa were added to 100 mL of sulphuric acid (1M) and then uniform solution was resulted by using magnetic mixer. Then, 1 mL fresh distilled aniline monomer was added to stirred aqueous solution. The reaction was carried out for 5 h at room temperature. Consequently, the resulted polymer was filtered on filter paper and to separate the oligomers and impurities, product was washed several times with deionized water and dried at room temperature.

### 2.4. Preparation of Polyaniline Nanocomposite

For preparation of PANI-PVA nanocomposite, 1 g ($(NH_4)_2S_2O_8$) was added to 100 mL of $H_2SO_4$ (1.0 M) and then a uniform solution was resulted by using magnetic mixer. Then, 0.4 g of PVA) was added to the solution and 1.0 mL fresh distilled aniline monomer was injected to stirred solution. The reaction was carried out for 5 h at room temperature. Consequently, the product was filtered to separate the impurities. Product was washed several times with deionized water and dried at temperature about 40 $^o$C in oven for 24 h.

## 3. Results and Discussion

### 3.1. Characterization of the Nanocomposites

The chemical method can be a general and useful procedure to prepare conductive polymers and their composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters [12]. Polyaniline has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation basis on the adsorption through nitrogen, which having one pair of electrons, is responsible for the technologically interest in chemistry and physics [20].

### *3.2. Morphology of PAn Nanocomposites*

The morphology of nanocomposites was studied, using scanning electron microscope (SEM).

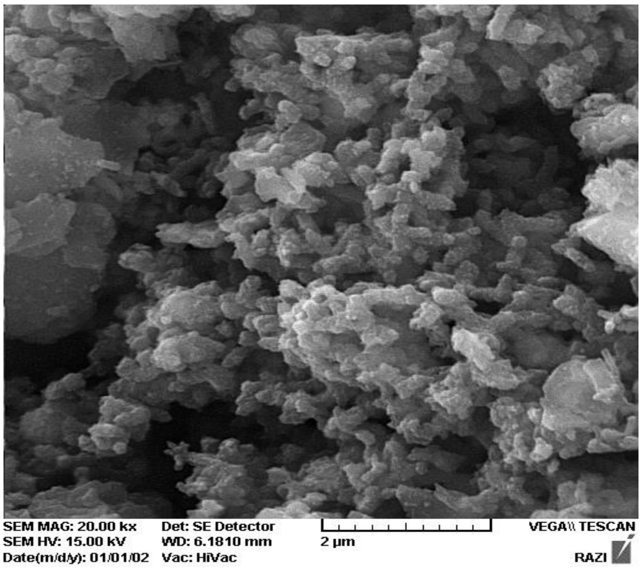

**Fig 1.** Scanning electron micrograph of PANI generated in aqueous media.
Reaction conditions: $(NH_4)_2S_2O_8$ = 10 g/L, aniline monomer 10.75× $10^{-2}$ mol/L, volume of solution 100 mL.

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters [25]. Polyaniline (PANI) has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which, having a lone pair of electrons, is responsible for the technologically interesting chemistry and physics.

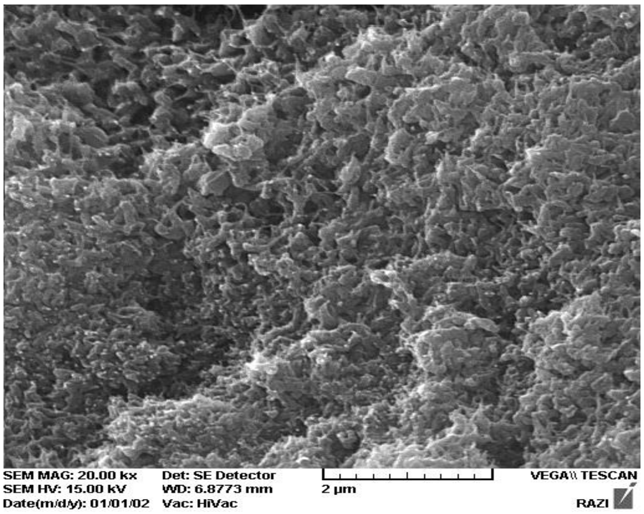

**Fig. 2.** Scanning electron micrograph of PAn/PVP in aqueous media.
Reaction conditions: $(NH_4)_2S_2O_8$ = 10 g/L, aniline monomer 10.75×$10^{-2}$mol/L, PVP= 4 g/L.

It is clear that surfactants disperses uniformly in the polyaniline matrix and leads to the formation of typical average grain size around 74 nm, which is consistent with the calculated results from XRD pattern and hydrothermal reaction process. The particles sizes of the nanocomposites have been listed in Table 1 [21]. The surface morphology of polymers was studied, using scanning electron microscope. As shown in Figs. 1 and 2, the size and homogeneity of particles are dependent on the type of surfactant. By comparison between Figs. 1-3, the results indicate that the surfactant strongly influence the particle size and homogeneity of particles. PAn particles synthesized without surfactant was shown in Fig. 1. As can be seen in micrographs, the nanocomposites obtained using surfactants of PVP, HPC, PVA, PEG and DBSNa exhibit spherical particles. It is apparent that using surfactant decreases the tendency to form agglomerates which leads to more homogeneous distribution, because surfactant prevent from gross aggregation of particles.

**Table 1.**
Preparation conditions and some properties of products.

| Type of solvent | Type of additive | Average particle size (nm) |
|---|---|---|
| Water | Pure polyaniline | 148 |
| Water | Polyaniline + HPC | 64 |
| Water | Polyaniline + PVP | 52 |
| Water | Polyaniline + PVA | 97 |
| Water | Polyaniline + PEG | 86 |
| Water | Polyaniline + DBSNa | 73 |

### *3.3. FTIR spectroscopy*

The chemical structure of obtained product was determined by FTIR spectrum. The FTIR spectroscopy has provided valuable information regarding the formation of polyaniline. FTIR analysis has been done to identify the characteristic peaks of product. Fig. 4 shows the FTIR spectra of pure polyaniline and polyaniline nanocomposite. The peak locations related to the corresponding chemical bonds are in a good agreement with those reported in the literature [26]. The main bands of protonated polyaniline, represented by the absorption bands at 1562 cm$^{-1}$ (C=C stretching vibration of the quinoid ring), 1475 cm$^{-1}$ (stretching vibration of C=C of the benzenoid ring), The peaks observed at 1302 cm$^{-1}$ (C-N stretching vibration), 1125 cm$^{-1}$ (C-H in-plane deformation), 804 cm$^{-1}$ is the characteristic of Para distributed aromatic rings, indicating polymer formation. It can be associated formation bands between polyaniline and nanocomposite. From the spectra it can be found that the peaks positions have small shifts compared to the pure polyaniline The bands at 1562, 1475, 1302,1125 and 804 cm$^{-1}$ were shifted to 1560, 1476, 1302, 1137 and 800 cm$^{-1}$, respectively in the PANI nanocomposite. It proves the interaction of surfactants with the different reaction sites of polyaniline.

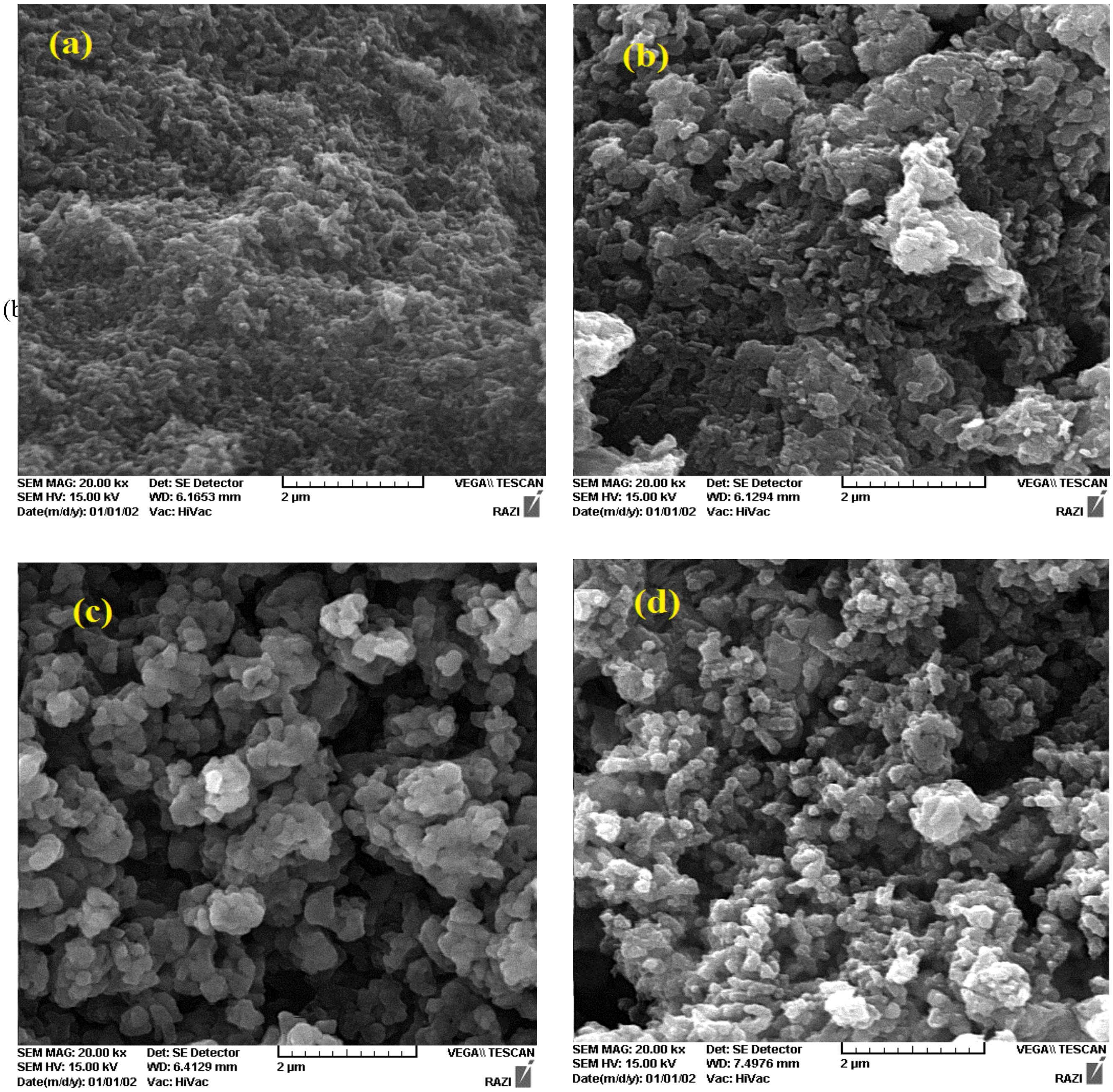

**Fig. 3.** Scanning electron micrograph of (a) PAn/HPC, (b) PAn/PEG, (c) PAn/PVA and (d) PAn/DBSNa in aqueous media. Reaction conditions: $(NH_4)_2S_2O_8$ = 10 g/L, aniline monomer $10.75\times10^{-2}$mol/L, HPC, PEG, PVA, DBSNa = 4 g/L

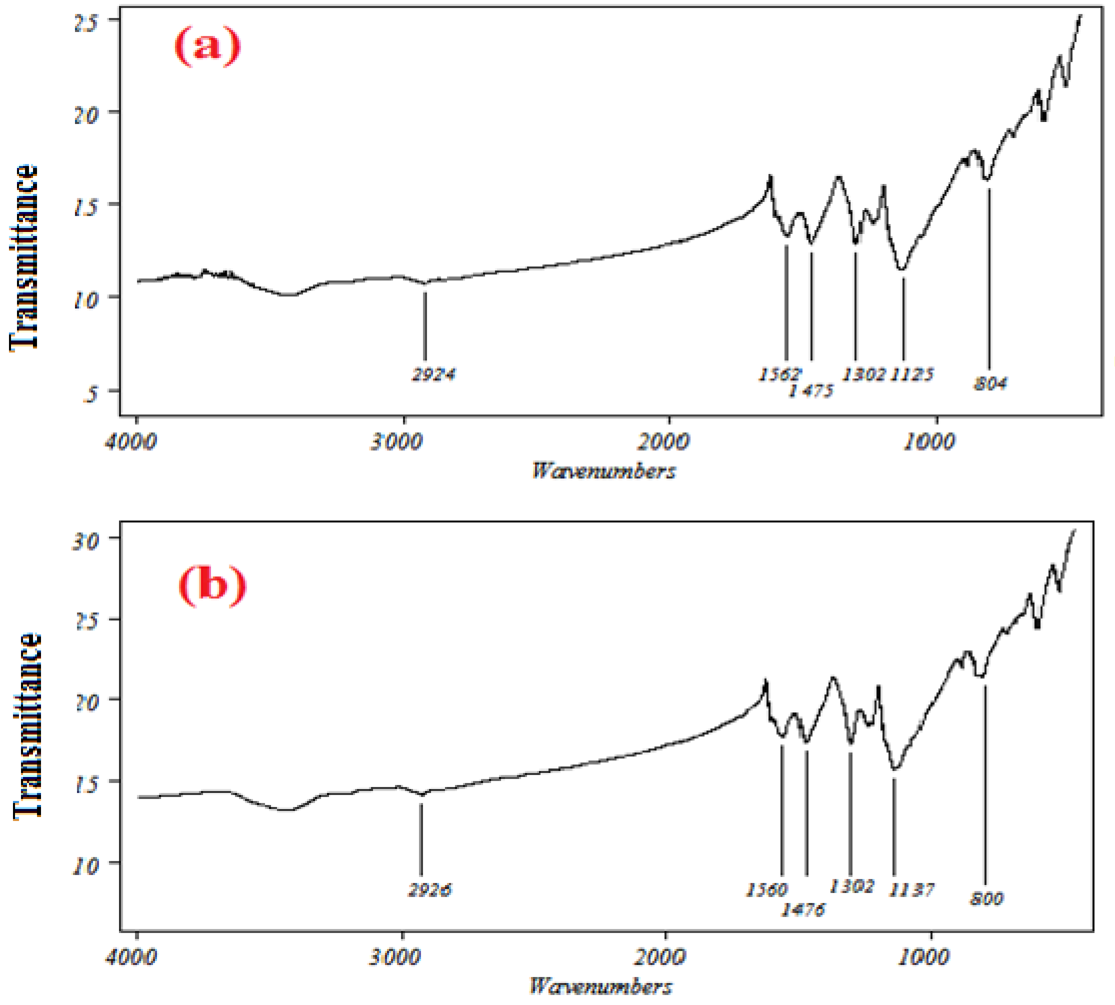

**Fig. 4.** FTIR spectra of (a) pure PAn, (b) PVP used as surfactant

### *3.4. X-ray diffraction study*

Polyaniline is inherently amorphous and hence there are no sharp peaks for polyaniline. The crystalline nature of nanocomposites is determined from XRD analysis. The XRD patterns of pure polyaniline and PANI nanocomposite have been shown in Fig. 5. All peaks in the XRD pattern are in agreement with the previous literature [27] and are indexed in the terms of the face-centered cubic (FCC) structure of surfactants. The main peaks in the XRD pattern of pure PANI are observed at 2θ = 17.8, 26.15 and 32.6° The characteristic peaks ascertained from the XRD pattern of PANI nanocomposite are at 2θ = 26.15, 33.25, 51.5 and 59.2° representing Bragg's reflections from (111), (200), (220) and (311) planes of the FCC structure of surfactants. The broad peak at 2θ = 26.15° is related to the diffraction of amorphous polyaniline. The diffraction peak at the 2θ = 26.15° of PANI nanocomposite isrelatively more intense compared to the polyaniline's one. The average crystallite sizes listed in Table 1 were estimated from broadening of the X-ray diffraction peak using the Scherrer's equation (1) [28]:

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where $\lambda$ is the X-ray wavelength (nm), k is the shape factor, D is the average crystallite size (nm), $\theta$ is the Brag angle (degree) and $\beta$ is the full width at half maximum of the diffraction peak (radian).

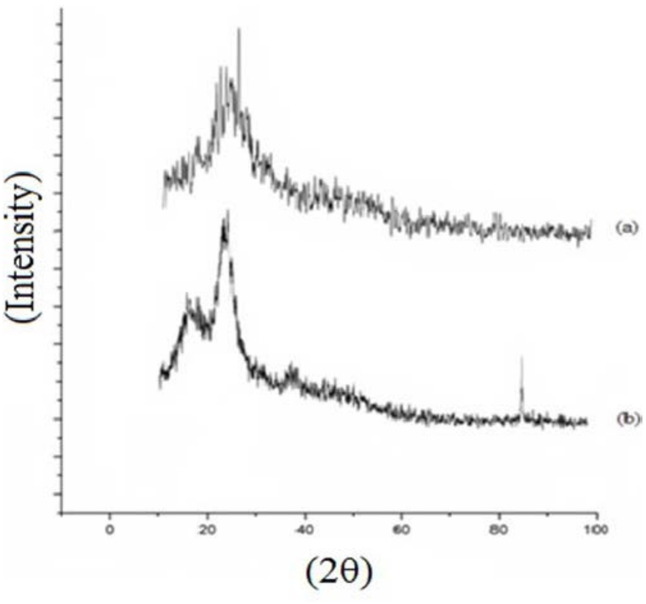

**Fig. 5.** XRD pattern of (a) PANI and (b) PANI nanocomposite, in aqueous media.

## 4. Conclusions

In this work, the characteristics of polyaniline nanocomposite, such as morphology and molecular structure were investigated in aqueous media using PVP as a surfactant. It was found that, the surfactant had a considerable effect on the morphology and particle size of resultant product which was probably due to the adsorption of surfactant. The SEM micrographs show that the surface active agent plays a major role on the surface morphology of product.

It was also found that the morphology, chemical structure and thermal stability depend on the polymerization conditions. The physical and chemical properties of the solution affect on the properties of the products. The molecular structures of the products were determined by FTIR spectroscopy. The results indicate that the intensities of the peaks are dependent on the surfactant, presumably because of the interaction of surfactant and polyaniline. FTIR spectroscopies show that PANI is available in the nanocomposites. The results of XRD confirmed the crystalline structure of PANI in the PANI nanocomposite.

## References

[1] Y. Sahin, S. Percin, M. Sahin, O. G. Alsancak, Electrochemical polymerization of fluoro-and chloro- substituted anilines and copolymers with aniline, J. Appl. Polym. Sci. 91 (2004) 2302–2312.

[2] B. Sanjai, A. Ragunathan, T.S. Natarajan, G. Rangarajan, Charge transport and magnetic properties in polyaniline doped with methane sulphonic acidand polyaniline-polyurethane blend, Phys. Rev. B. 55 (1997) 10734-10739.

[3] R. Brydson, H. Sauer, W. Engel, J. M. Thomass, E. Zeitler, N. Kosugi, H. Kuroda. Electron energy loss and X-ray absorption spectroscopy of rutile and anatase: a test of structural sensitivity, J. Ph. Con. Matt. 4 (1989) 797-782.

[4] K. Lee, S. Cho, S.H. Park, A.J. Heeger, C.W. Lee, S.H. Lee, Metallic transport in polyaniline, Nature. 441 (7089) 65-68.

[5] M. Chipara, D. Hui. P.V. Notingher, M.D. Chipara, K.T. Lau, J. Sankar, D. Panaitescu, On polyethylene–polyaniline composites, Composites. B. 34 (2003) 637-645.

[6] P. S. Rao, D. N. Sathyanarayana, Inverse emulsion polymerization: a new route for the synthesis of conducting polyaniline, Synth. Met. 138 (2003) 519–526.

[7] S. Li, Y. Cao, Z. Xue, Soluble polyaniline, Synth. Met. 20 (1987) 141–149.

[8] S. P. Armes, J. F. Miller, B. Vincent, Aqueous dispersions of electrically conducting monodisperse polypyrrole particles, J. Colloid. Interface. Sci. 118 (1987) 410–416.

[9] S. P Armes, M. Aldissi, Preparation and characterization of colloidal dispersions of polypyrrole using poly (2-vinyl pyridine)-based steric stabilizers, Polymer. 31 (1990) 569–574.

[10] Y. Cao, J. Qiu, P. Smith, Effect of solvents and co-solvents on the processibility of polyaniline: I. Solubility and conductivity studies, Synth. Met. 62 (1995) 187–190.

[11] W. Zheng, M. Angelopoulos, A. J. Epstein, A. G. MacDiarmid, Experimental evidence for hydrogen bonding in polyaniline: mechanism of aggregate formation and dependency on oxidation state, Polym. 30 (1997) 2953–2959.

[12] T. Hassani, H. Eisazadeh, Removal of Cd (II) by using polypyrrole and its nanocomposites, Synth. Met. 175 (2013) 15–20.

[13] H. Eisazadeh, H. R. Khorshidi, Preparation and characterization of polyaniline-DBSNa/$Fe_2O_3$ and polyaniline-DBSNa/CuO nanocomposites using surf active dopant sodium dodecylbenzenesulfonate (DBSNa), J. Vin. Add. Tech. 16 (2010) 105-110.

[14] Y. I. Tarasevich, V. Goncharuk, V. Polyakov, D. Krysenko, Z. Ivanova, E. Aksenenko, M.Y. Tryfonova, Efficient technology for the removal of iron and

manganese ions from artesian water using Clinoptilolite, J. Ind. Eng. Chem. 18 (2012) 1438-1440.

[15] M. Porramezan, H. Eisazadeh, Fabrication and characterization of polyaniline nanocomposite modified with $Ag_2O$ nanoparticles, Composites B: Eng. 42 (2011) 1980-1986.

[16] M. Hallajiqomi, H. Eisazadeh, M. Hosseini, H. Azizi Namaghi, Manganese removal from aqueous media using polyaniline nanocomposite coated on wood sawdust, Synt. Met. 194 (2014) 153-159.

[17] H. Eisazadeh, Removal of arsenic in water using polypyrrole and its composites, W. Appl. Sci. J. 3 (2008) 10-13.

[18] M. Ghorbani, M.S. Lashkenari, H. Eisazadeh, Application of polyaniline nanocomposite coated on rice husk ash for removal of Hg (II) from aqueous media, Synthetic Metals, 161 (2011) 1430-1433.

[19] J. Stejskal, I. Sapurina, M. Trchova, E.N Konyushenko, Oxidation of aniline: polyaniline granules, nanotubes, and oligoaniline microspheres, Macromolecules, 41 (2008) 3530-3536.

[20] P. K. Khanna, N. Singh, S. Charan, A. K. Viswanath, Synthesis of Ag/polyaniline nanocomposite via an in situ photo-redox mechanism, Mater. Chem. Phys. 92 (2005) 214-219.

[21] H. Eisazadeh, M. Ghorbani, Copolymerization of pyrrole and vinyl acetate in aqueous and aqueous/nonaqueous media, J. Vin. Add. Tech. 15 (2009) 204-210.

[22] M. Ghorbani, H. Eisazadeh, R. Katal, J. Vin. Add. Tech. 16 (2010). 217-221.

[23] K. R. Reddy, K. P. Lee, Y. Lee, A. I. Gopalan, Mater. Lett. 62 (2008). 1815-1818.

[24] J. H. Kim, F. F. Fang, H. J. Choi, Y. Seo, Mater. Lett. 62 (2008). 2897-2899.

[25] M. V. Kulkarni, A. K. Viswanath, R. Marimuthu, T. Seth, Polym. Eng. Sci. 44 (2004). 1676-1681.

[26] H. P. Klong, L. E. Alexander, Wiley (1959). 491-539.

[27] A. Gök, M. Omastová, J. Prokeš, Eur. Polym. J. 43 (2007). 2471-2479.

[28] T.W. Webi, R.K. Chakravort, AIChE J. 20 (1974). 228-236.