Original Research article

Hydrothermal Synthesis of Poly (Aniline-co-Sulphanilic Acid) Copolymer with Highly Improved Electrical Conductivity and Ion Exchange Properties

Sanjay R. Thakare[a, *], Mangala R. Pal[b]

[a] Department of Chemistry, Goverment Institute of Forensic Science, Civil Line, Nagpur 440001, India

[b] Department of Chemisty, Pandav College of Engineering and Technology, Nagpur 440024, India

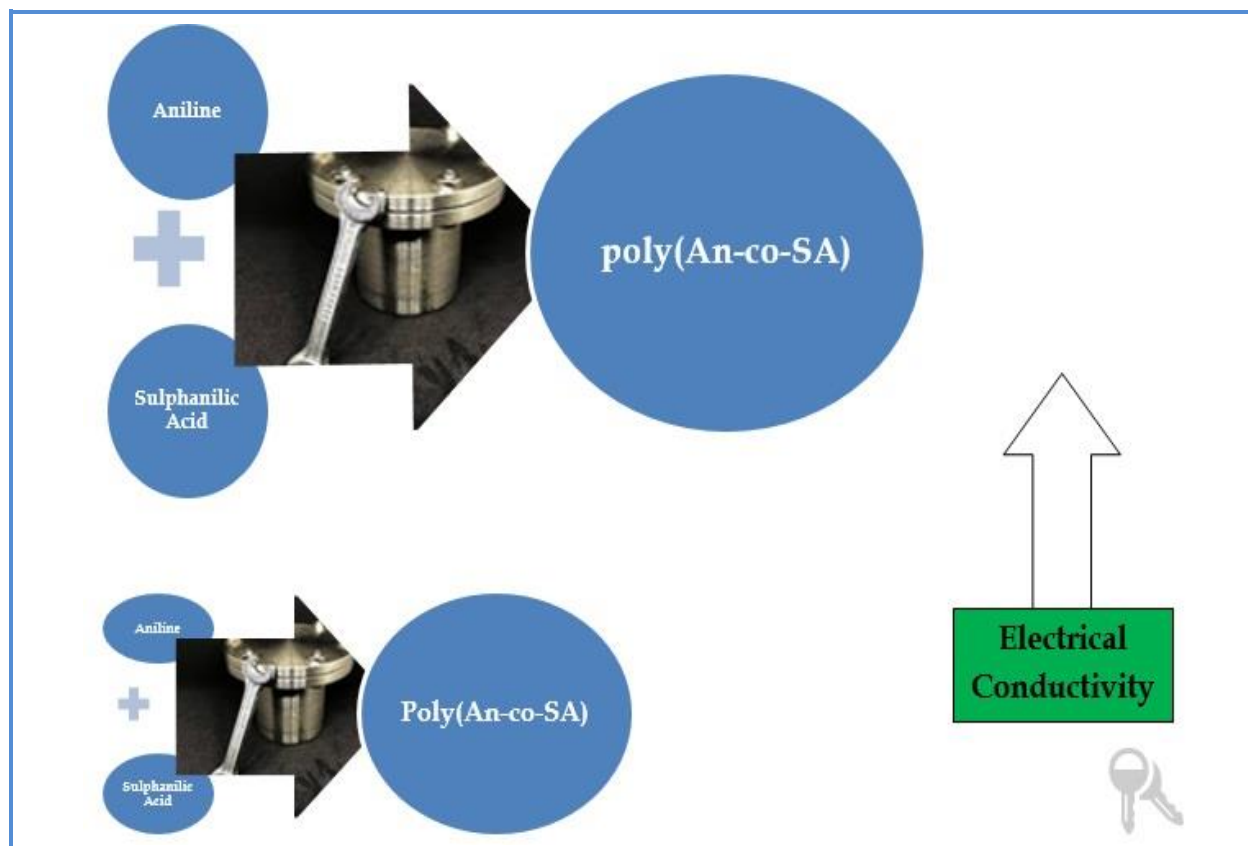## ARTICLE INFORMATION

ABSTRACT

Facile and fast hydrothermal copolymer synthesis of aniline and sulphanilic acid was studied at the presence of ammonium persulphate as an oxidising agent for polymerisation reaction of 1:1 mole ratios of aniline to sulphanilic acid. Physiochemical properties of poly (An-co-SA) copolymer micro particles were scientifically analyse using numerous key techniques. The toxic metal ions spontaneous subtraction efficiency of the poly (An-co-SA) copolymer micro particles was optimized. Results recommended that, the properly controlling the polymerization under the hydrothermal method was a simple but helpful way to significantly improve the conductivity of the copolymers of aniline and sulphanilic acid monomer copolymerized. The poly (An-co-SA) copolymer micro particles could be very appropriate to exclusion and revitalization of metal ions which was toxic to environment from wastewater.

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*Corresponding author: E-mail: sanjaythakare@yahoo.co.uk, Department of Chemistry, Govt. Institute of Forensic Science, Civil Line, Nagpur 440001. India, Tel: +919011097694; Fax: +98712-2534504

Graphical Abstract

Introduction

Polymers are important class of material among the scientists due to their simple synthesis process, high chemical stability, conductivity like to that of metals and various application [1-7]. Polyaniline is among the one received considerable attentions recently due to its budding applications in electronics, sensors and batteries. Synthesis of self-doped polyaniline is an important mile stone in the field of polymers which conduct electricity due to its desirable properties to design the material for specific applications [8]. Enhancement of solubility, good redox action and desired electrical conductivity in broad range of pH [9] of self-doped polyaniline makes more desirable material for the design of energy conversion devices, sensors, elctrochromic devices, electronic circuits and many more [10-11]. It was reported that the preparation method and composition of solution greatly affect the physiochemical properties of polyaniline [8]. In situ generation of protons with simultaneous oxidation of molecular hydrogen present in solution oxidized aniline electrolytically gives polyaniline having better conductivity and faster film formation was reported by Pekmez *et al.* [12]. Aniline in hydrogen saturated acetonitrile solution oxidized at presence of 25 mM Cu^+ ions

gives polyaniline a conductivity of 10 S/cm [13]. Polyaniline with $-SO_3H$ group (SPAN) was a water soluble and no need to external doping polymer reported first time [13]. SPAN is motivating in view of its distinctive electro active properties in an ample choice of solutions. The solubility of SPAN makes the material easily processable for variety of applications [14-18]. SPAN conductivity not depend on external protonation in expansive pH range was also reported. Environmental stability of the SPAN was improved due to removal of electron property of $-SO3-$ group and showed superior thermal stability compared with that of the hydrochloric acid-doped polyaniline [14]. $-SO_3^-$ groups attached with polymer backbone covalently and behave like anions in a solution. Therefore, there is no need for external dopant anion when $-SO_3^-$ groups present in a polymer structure [14].

SPAN with $-SO_3^-$ groups as counter ions was obtained by three methods. Electrochemically or chemically obtained polyaniline was treated with fuming H_2SO_4 in water to obtain a SPAN [19]. Chlorosulfonic acid along with sulfur trioxide/tri ethyl phosphate complex to obtain a SPAN was also reported [20]. SPAN was also prepared by copolymerization of aniline or its derivatives with metanilic acid [21–25], orthanilic acid [26-28], 2,5-diamino benzene sulfonic acid [29] either by chemically or electrochemically. Aniline sulfonic acid was also used as a monomer to prepare fully-sulfonated polyaniline. The oxidative polymerization of *o*-amino benzene sulfonic acid or *m*-amino benzene sulfonic acid was noticeably offer fully sulfonated SPAN but attempts so far by both chemical and electrochemical methods [30] was unproductive, seemingly because of steric obstruction and the powerful deactivate persuade of the electron removing sulfonic acid group. Inclusion of methoxy functional group having electron donating power onto the monomer does; however, allow oxidative polymerization and poly (3-amino-4-methoxyben-zenesulfonic acid) was prepared in this way [31] and has found applications for electron device fabrication [32]. The room-temperature conductivity of this methoxy-SPAN is, however, significantly less than that for 50 or 75% sulfonated SPAN [31-32] which has been attributed to the larger twist of the phenyl rings and increased inter chain separation. Another way of obtaining soluble polyaniline is to dope with another polymer which contains acidic units such as a poly (styrene sulfonic acid) [33–35], poly (3-sulfonato-4-hydroxystyrene) [36], nafion [37] or to dope with organic sulfonic acids such as camphor sulfonic acid [37], a sulfo acid. High pressures oxidative polymerization of ortho and meta derivative of amino benzene sulfonic acid [39] to obtained SPAN was reported which was soluble in water, electrically conducting and no external dopant required. The aniline addition as a monomer increased the product yield up to 100% was explained in detail.

Kaner *et al.* [40] successfully synthesized various sulfonated polyaniline (SPAN) nanostructures *via* rapid initiated copolymerization of *o*-amino benzene sulfonic acid and aniline or its derivatives in the presence of *N*-phenyl-*p*-phenylene diamine as a catalyst in an acidic medium. The SPAN nanostructures can be easily processed in many solvents, revealed higher conductivity at pH values of 5.5–6.0 compared with their polyaniline counterparts (10^{-2} S/cm vs 10^{-8} S/cm). Despite of, numerous scientists examine the preparation of water soluble polyaniline derivatives using different approaches, most of which are expensive and not suitable for large scale use [41-43]. Till date, sulfonation of polyaniline, in which the polyaniline emeraldine salt of was interacted with inert solvent solution of chlorosulfonic acid, has been the most common method to improve the solubility and processability of polyaniline in water [44-46]. The sulfonated polyaniline (SPAN) prepared using this method was soluble in water from acidic to basic pH of solution. However, owing to the occurrence of strong electron removing nature of $-SO_3H$ groups, the conductivity of SPAN reduces to some extent compared to that of pure polyaniline [47]. Easy to operate and economical viable nature of this method attract the scientific groups to prepare SPAN by this method generally.

On the basis of earlier study and importance of SPAN, we now present the first report of a facile preparation of fully sulfonated SPAN by oxidative polymerization of aniline and amino benzene sulfonic acid under the influence of high pressures in the liquid phase generally referred as hydrothermal condition.

Experimental

Preparation of 0.4 M aniline, 0.4 M of sulphanilic acid and 0.4 M ammonium persulfate aqueous solutions were prepared. 50 mL volume of all three-solution taken together in Teflon line autoclaved and immediately closed the vessels. The vessel was kept in preheated oven at 110 °C for 4 h. After 4 h vessel remain kept in the oven and cooled in natural way overnight. Next day filter the solution on suction pump. Dark greenish colour co-polymer was washed with distilled water, then with 50% methanol solution several times until the filtrate become colourless. After washing the copolymer was dried out in oven at 60 °C temperature in absence of air for overnight and product hereafter designated as poly (An-co-SA). Similar method of preparation described above was also applied for 2:1 and 3:1 proportion of sulphanilic acid to aniline copolymer preparation. The solid product was not obtained in case of 2:1 and 3:1 molar proportion of poly (An-co-SA) may be because of increase of concentration of sulphanilic acid increase the solubility of the copolymer or increase of steric repulsion.

Interaction of light and subsequently the absorption of UV-visible light by material was measured using the double beam UV-vis spectrophotometer (Model-Shimadzu UV-1800). The solutions of the sample in dimethyl sulfoxide (DMSO) were used for recording the spectra. FTIR spectrums were taken using the Perkin-Elmer RXI spectrophotometer by the KBr pellet technique. The electrical conductivity (direct current) of poly (An-co-SA) was measured at 30 °C by applying four probe methods using a keithley instrument. The thermogravimetric analysis (TGA) was recorded up to 1000 °C using diamond model of Perkin-Elmer TGA/DTA in argon atmosphere at a heating of 10° min. The morphological images were recorded by JEOL JSM 5600 L scanning electron microscope. XRD patterns of the materials were recorded using XRD Philips PW-1700 X-ray diffractometer. Analytical grade reagents were used in experimental studies. Certain concentrations of synthetic solutions were prepared using nitrate salts of test metals (Zn $(NO_3)_2 \cdot 6H_2O$, Cu $(NO_3)_2 \cdot 6H_2O$ and Ni $(NO_3)_2 \cdot 6H_2O$ from Merck) in 1:1 ammonia water solution. The prepared copolymer is insoluble in ammoniacal solution. pH adjustments were carried out by using 0.1N HCl and 0.1N NaOH.

Results and discussion

Figure 1. illustrates the XRD pattern of the poly (An-co-SA) having ratio 1:1. The product obtained by hydrothermal method is polycrystalline rather than crystalline. In addition to the broad bands, the peak at 6°, 18° and 26° which are ascribed to the repeated parallel and perpendicular polymer chains of polyaniline, respectively. It was reported that the crystallinity of polymers of aniline doped with sulphanilic acid depends on the size of dopant and protonation level and greatly affect due to ring substitution which increases the space hindrance to the internal rotation of the chain. The XRD spectrum of poly (An-co-SA) was like to amorphous indicates the insertion of sulphanilic acid in the chain structure of polymer which hinders the internal rotation.
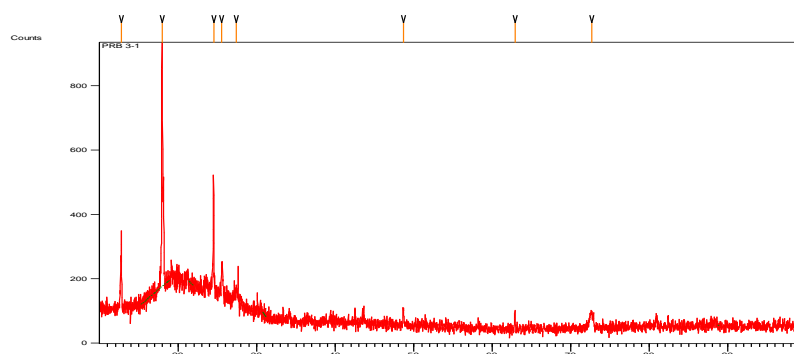

Figure 1. XRD spectra of copolymer poly (An-co-SA)

The UV-vis spectra of poly (An-co-SA) prepared by hydrothermal method exhibited more resemblance to the spectral features of aniline (Figure 2). It was reported that the 326 nm, 433 nm, 630 nm, and 820 nm absorption peaks were observed for spectrum of salt of polyaniline with HCl in DMSO solvent. Π–Π* transition of electron was ascribed at 326 nm wavelength of maximum in the spectrum and represent the degree of conjugation [48]. In the spectrum of the copolymer, this band was observed intense. The second absorption band at 540–630 nm was recognized to an exciton transition (n– Π*) from the HOMO of benzenoid ring (lone pair, nonbonding nitrogen) to the LUMO (Π*) of quinoid ring [49]. The remaining two weak absorptions at 430 nm and 830 nm have been assigned to the polaron transitions of the conducting form of polyaniline [50] and they indicate the presence of the protonated form of polyaniline in the poly (An-co-SA). The spectra of poly (An-co-SA) exhibit two bands near 260 and 300 nm with 1:1 sulphanilic acid aniline in the poly (An-co-SA). The exciton band near 630 nm undergoes a large hypsochromic shift when the amino benzene sulfonic acid as a dopant suggests a decrease of degree of conjugation. The neighbouring phenyl rings of copolymers may have larger torsion angle with reference to the plane of nitrogen atoms because of steric repulsion between the sulfonic acid group and the hydrogen of neighbouring phenyl rings [17]. The band at 300 nm in the polyaniline salt shifts to 285 nm in the spectra of the poly (An-co-SA), indicating once again a decrease in the extent of conjugation due to the interactions between OSO_3H and NH_2 favouring chelate formation, as observed for sulfonated polyaniline [19].
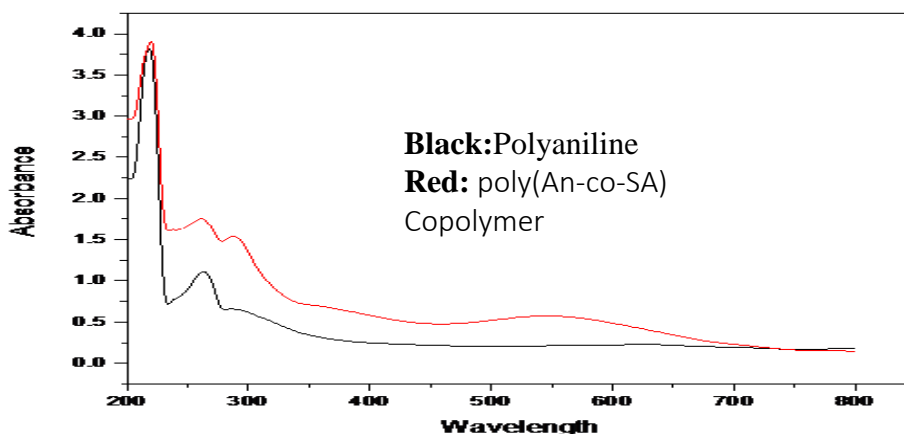

Figure 2. Absoption spectrum of copolymer poly (An-co-SA) and polyaniline

FTIR analysis of poly (An-co-SA) prepared by hydrothermal method was represented in the Figure 3. A broad band at 3442, 3473, 3449, 3441 and 3717 cm^{-1} assigned to the free N-H stretching

vibrations and absorbed water. The band at 2947, 2884, 2943 and 2951 cm^{-1} show the aromatic C-H stretching. The ring stretching vibration of quinoid (N=Q=N) analogous absorption was examined at 1575 and 1574 cm^{-1}. The characteristic peaks at 1400 cm^{-1} corresponds to benzenoid (N-B-N) in co-polymer was observed. C-N stretching band of an aromatic amine appeared at 1318 cm^{-1} and 1299 cm^{-1} indicate the long chain length of the polyaniline. The peaks at 1035-1040 cm^{-1} is caused by (S=O) stretching confirms the presence of sulfonate groups in poly (An-co-SA). The S-O stretching peaks at 688 cm^{-1} and peaks at 633 cm^{-1} represents C-S stretching vibration in poly (An-co-SA). The peak at 1040, 688 and 633 cm^{-1} of poly (An-co-SA) spectrum was constituent with the presence of –SO$_3$H group link to the aromatic ring.

Figure 3. FTIR spectrum of copolymer poly (An-co-SA)

The TGA profiles of the poly (An-co-SA) are demonstrated in Figure 4. Poly (An-co-SA) showed three-step degradation in thermogravimetric analysis. The first step starts from room temperature to 150 °C, suggested a detachment of water molecule in the form of moisture associated with polymer matrix. The second stage loss is from 150 to 350 °C, which associated with the loss the dopant ion from the polymer matrix. The weight loss after 350 °C is due to the complete degradation and decomposition of the polymer backbone after the loss of dopant ion.

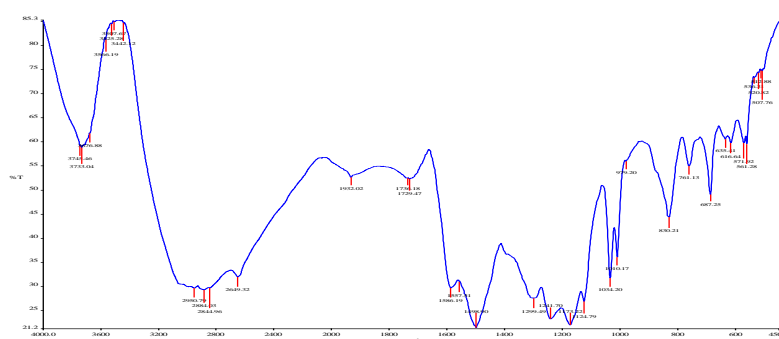**Figure 4.** Thermal degradation pattern of copolymer poly (An-co-SA)

Figure 5. reveals the SEM image of the poly (An-co-SA) by hydrothermal method. The particles of copolymer were irregular spherical with the diameter about 500 nm and aggregated together. EDX analysis confirmed formation of the copolymer having aniline and sulphanilic acid. EDX data in tabulated form and elemental analysis is given in the supplementary information. The EDX analysis and elemental analysis supported formation of the copolymer.
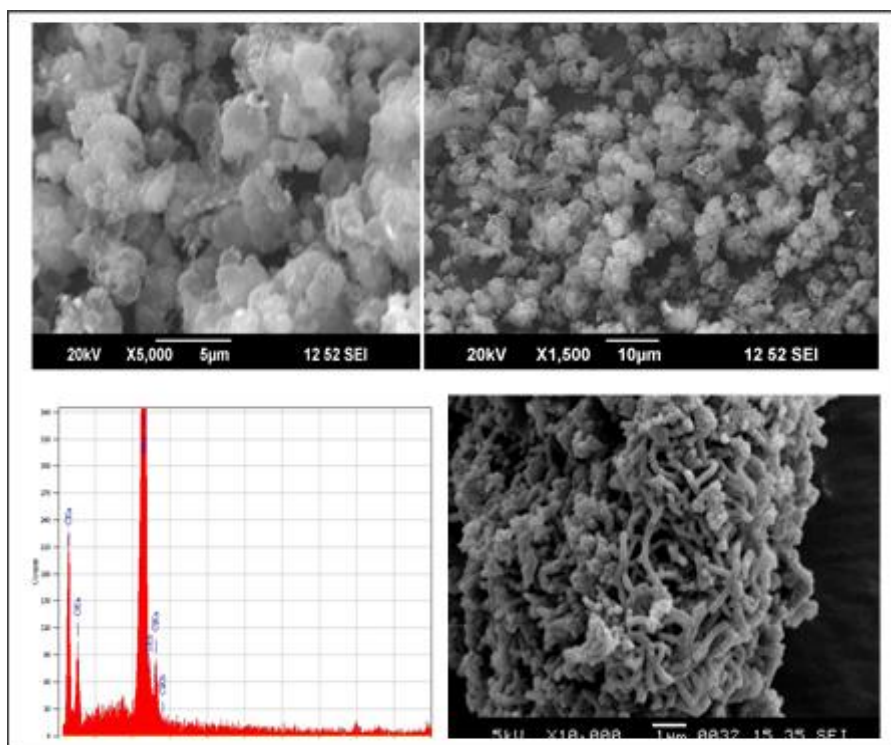

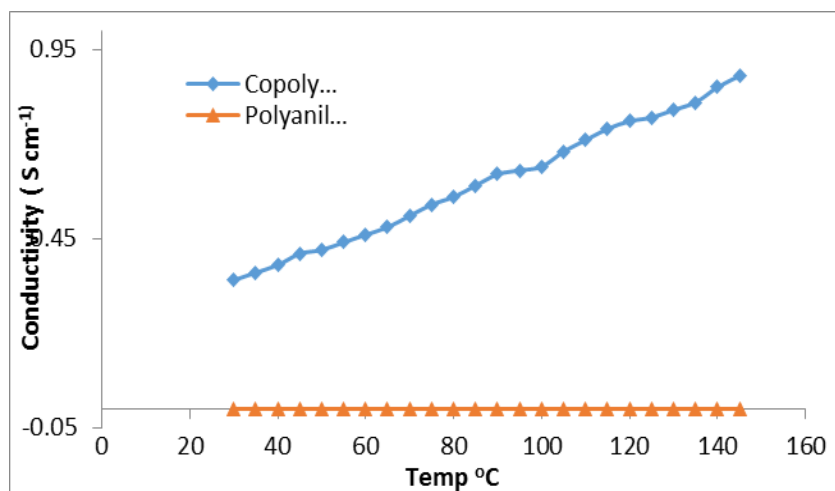**Figure 5.** SEM images with EDX of copolymer poly (An-co-SA)

Figure 6. Electrical conductivity study of copolymer poly (An-co-SA) with temperature and polyaniline

Self-doped polyaniline typically exhibits conductivity of 10^{-6}–10^{-1} S/cm^{-1} [19]. The poly (An-co-SA) obtained by hydrothermal method having a room temperature electrical conductivity was 0.34 S/cm^{-1} and electrical conductivity was increases with the variation of temperature higher side linearly. This indicate that the material behaves like a semiconductor and have a higher conductivity than the polyaniline prepared by hydrothermal method. The results are represented in Figure 6.

Many environmental problems were associated with discharge of huge quantity of toxic metal in to body of environment. Toxic metals were non-biodegradable and easily accumulated in nature and hence notable than the other pollutants. Their presence was exceeding than the optimum limit caused diseases and disorder to the living animals [51-53]. Acute toxicity and non-biodegradable nature of zinc makes one of the priority pollutants in aqueous medium. Hence zinc containing waste was considered as hazardous waste [51]. Nickel was another heavy metal and priority pollutants in the nature and widely used in industrial process gains importance of removal from wastewater [52]. Nickel in the form of nickel sulphate salt was used in a many industry affect the application of desired treatment method for the removal from wastewater [53]. Precipitation method, electrolysis, ion exchange technology, evaporation techniques and adsorption technology were generally used for the management of toxic metals from the wastewater [54-55]. High efficiency and low operational cost of ion exchange method makes a smarter treatment process of wastewater among the other treatment processes. More recovery of metal, higher selectivity, low volume of sludge and follow the accurate discharge specification are the advantages of the ion exchanges method [56].

The efficiency of ion exchange process was affected by a pH of solution which was significant consideration because hydrogen ion was a strong competitor as an adsorbate and solution pH influence the functional groups ionization. To assess the consequence of pH on removal of nickel copper and zinc by poly (An-co-SA), a 100 mL of 100 mg/L metal solutions were used. All experiments were carried out in the 2–9 pH of solution. Constant poly (An-co-SA) amount (0.5 g) was added to all reaction bottles and solutions were agitated for 1 h at 200 rpm speed. Consequence of pH on removal efficiency is shown in Figure 7. As seen from Fig. 7, the optimal uptake of Ni^{2+}, Cu^{2+} and Zn^{2+} occurred at pH ranges from 4 to 7. Decrease of removal efficiency achieved by poly (An-co-SA) can be described with formation of metal hydroxide during reaction of nickel, copper and zinc metal ions with OH^- at higher solution pH.
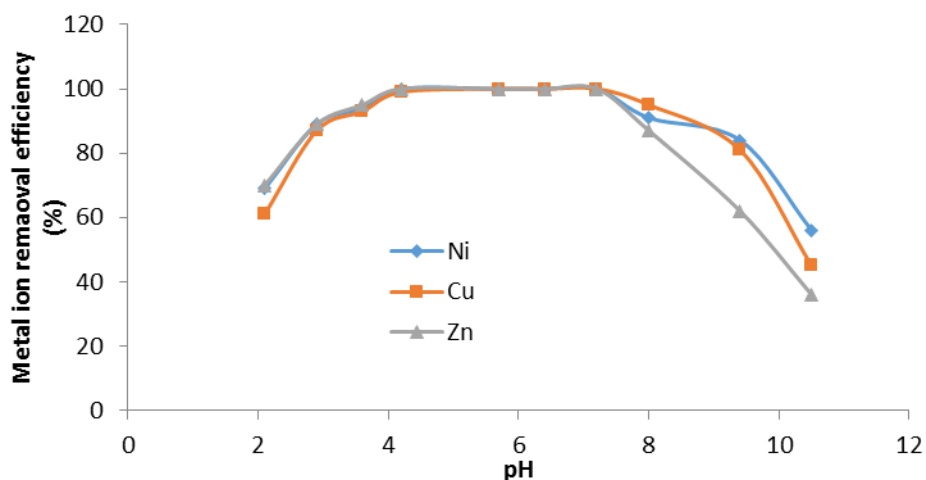
Figure 7. Influence of pH on removal efficiency of copolymer poly (An-co-SA) for Ni^{2+}, Cu^{2+} and Zn^{2+} ions

Amount of polymer required for the quantitative subtraction of metal ions was an important parameter for the application of ion exchange technology. The faith of metal removal by poly (An-co-SA) was examined by altering the quantity of poly (An-co-SA) (0.25–1.0 g), while the other parameters such as pH (pH 7.2 + -0.05 for all metals), initial metal concentration (100 mg/L) and stirring speed (200 rpm) remained constant. As seen in Figure 8, the adsorption percentage of metal ions increased with higher poly (An-co-SA) dosages and the removal efficiency of 100% was achieved by using 0.75 g/100 mL poly (An-co-SA) dosage for all metal ions. This result proved that increasing the amount of adsorbent provides higher removal due to formation of greater adsorption sites
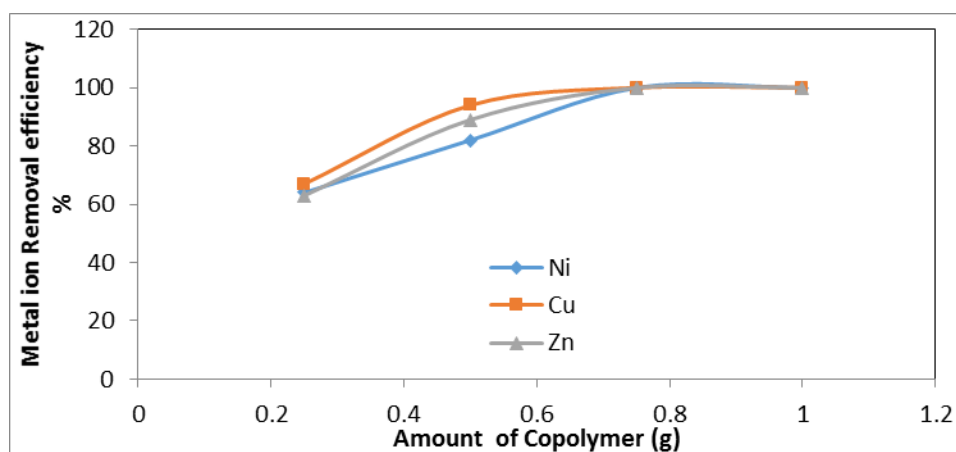

Figure 8. Adsorption efficiency of copolymer poly (An-co-SA) for Ni^{2+}, Cu^{2+} and Zn^{2+} ions

Conclusion

Copolymer of sulphanilic acid and aniline were prepared using a simple and less time-consuming hydrothermal method. The characterization of poly (An-co-SA) was carried out by different techniques such as XRD, UV-visible absorption spectroscopy, FTIR, TGA and SEM analysis. It was found that the prepared copolymer had first-class ion exchange properties, so it was further used for some environmental application. Copolymer poly (An-co-SA) material was good enough to exchange the metal ion such as Ni^{2+}, Cu^{2+} and Zn^{2+} and order is $Ni^{2+}>Cu^{2+}>Zn^{2+}$.

Conflict of Interest

 We have no conflicts of interest to disclose.

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