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# Removal of cations using ion-binding terpolymer involving 2-amino-6-nitro-benzothiazole and thiosemicarbazide with formaldehyde by batch equilibrium technique

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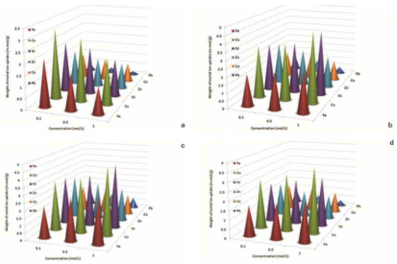
## HIGHLIGHTS

- A novel [(2-amino-6-nitro-benzothiazole)–thiosemicarbazide–formaldehyde] terpolymer has been synthesized.
- SEM images show high porosity in the surface of the resin evidences the effective adsorption of various metal ions.
- BTF terpolymer is a well recyclable cation-exchange resin for industrial waste water treatment.

## GRAPHICAL ABSTRACT

Effect of (a) NaCl, (b) NaNO$_3$, (c) NaClO$_4$ and (d) Na$_2$SO$_4$ electrolytes on metal ion uptake.



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## ABSTRACT

2-Amino-6-nitro-benzothiazole and thiosemicarbazide with formaldehyde (BTF) terpolymer was synthesized by the condensation polymerization technique. The elemental analysis and physico-chemical parameters of the terpolymer were measured. This chelation terpolymer was characterized by infrared, electronic and nuclear magnetic resonance ($^1$H & $^{13}$C NMR) spectral studies. The molecular weight of the terpolymer was determined by gel permeation chromatography (GPC). Surface analysis of the terpolymer was analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) method. The thermal stability of the terpolymer was analyzed by thermogravimetric analysis (TGA). The cation-exchange property of the terpolymer was determined by batch equilibrium method with the effect of pH, contact time and electrolytes. The reusability of the resin was also studied to estimate the effectiveness of the terpolymer resin.

## 1. Introduction

The treatment of industry wastes has been a strong concern as it continues to grow day by day. One category of such industrial pollutants includes heavy metals, often contained in the wastewater. When released into the environment, these metals can cause severe damage to the human body, including accumulative poison, brain damage, and cancer [1]. Several processes were accessible for heavy metal removal, including chemical precipitation, membrane, and retention technique [2–4]. An effective technique to separate the selective metal ions from wastes was greatly found to be ion-exchange process. Ion-exchange resins are polymers that can reversibly interchange the counter ions. The resins are organized into two main types depending upon the charge of the counter ions with which they can exchange. The cationic exchangers contain the negatively ionizable group which is capable of interchanging the positively charged or cationic counter ion. The anionic exchange resin interchanges the negatively charged or anionic

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counter ion due to the existence of the positively ionizable group. Polymeric resin was synthesized and reported for its tremendous ion-exchange characteristics towards selective metal ions *viz.* $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$ and $Co^{2+}$ [5]. Tannin–phenol–formaldehyde resins produced using tannin from dried fruit of *Terminalia chebula* found to have highest metal ion adsorption capacity against selective alkaline earth such as $Ca^{2+}$ and $Mg^{2+}$ and transition metal ions [6]. *O*-Nitrophenol/thiourea/formaldehyde and anthranilic acid/thiourea/formaldehyde terpolymers were synthesized and reported as excellent chelating ion-exchangers for the separation of metal ions from the waste solutions [7,8]. Dithiocarbamate styrenic resins possess very high adsorption capacity and also a faster way of adsorption with $Zn^{2+}$ and $Cd^{2+}$ metal ions [9]. An eco-friendly technique was employed to synthesize a terpolymer and it seizes excellent metal ion binding capacity with the various chosen metal ions and reported [10]. Recently by our research group, various terpolymers have been synthesized and reported for their chelating ability with several metal ions and also the resins have more porous in the structure which was responsible for the high adsorption capacity towards the chosen metals [11,12]. Bisphenol–guanidine–formaldehyde terpolymer resin was synthesized and reported as a selective ion-exchanger due to the presence of nitrogen atom containing guanidine [13]. 8-Hydroxyquinoline and salicylic acid with formaldehyde resin have been synthesized and investigated for its ion-exchange property. The resin was found to have more capacity to bind with the selected metal ions and hence reported as an excellent chelating resin for transition and post-transition metal ions [14]. Batch equilibrium method was employed to study the ion-exchange property of the terpolymer involving 2,4-dihydroxyacetophenone, biuret and formaldehyde and from the results, it was observed that the ion-exchange capacity of the resin increases as the pH also increases [15]. Chelating resins have high thermal resistance also can be used as semiconducting devices and electronic devices. The results of thermogravimetric analysis of anthranilic acid and formaldehyde with *m*-cresol terpolymer show high thermal stability [16]. Similarly the resin derived from salicylic acid, formaldehyde and resorcinol was reported for its high thermal resistance and the thermodynamic parameters of the polymer [17]. Salicylic acid, guanidine and formaldehyde were subjected to polycondensation to yield a terpolymer which showed high thermal stability when investigated with the effect of heat [18]. Thermogravimetric study of 8-hydroxyquinoline 5-sulphonic acid and melamine with formaldehyde resin showed that the polymer was thermally stable compound even at high temperature [19].

In the present investigation, the terpolymer resin derived from 2-amino-6-nitrobenzothiazole and thiosemicarbazide with formaldehyde was synthesized and characterized by FTIR, UV–vis, $^{1}H$ & $^{13}C$ NMR, GPC, SEM, XRD and TGA. The ion-exchange property of the terpolymer was evaluated by batch equilibrium technique.

## 2. Experimetal

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade.

### 2.1. Synthesis

2-Amino-6-nitro-benzothiazole (0.05 M) and thiosemicarbazide (0.05 M) with formaldehyde (0.1 M) was taken as monomers in a clean round bottom flask equipped with stirrer and a refluxed condenser using dimethyl formamide medium. The mixture was refluxed in an oil bath at 150 ± 2 °C with constant stirring for 6 h [20]. After the reaction time, the mixture was cooled and the obtained precipitate was separated out by filtration and washed with hot water, ether and methanol to remove the unreacted monomers and then re-crystallized using tetrahydrofuran. The reaction sequence of the synthesis of BTF terpolymer is shown in Scheme 1.

### 2.2. Instruments

The physico-chemical properties such as moisture content, solid percentage, void volume fraction, true density and sodium exchange capacity of the terpolymer were calculated as per the reported procedure [21]. The dry resin of 20–40 meshes size particles was used for the characterization. The elemental analysis was carried out on Elementar instrument, Model Vario EL III, Germany. The molecular weight of terpolymer was determined by GPC "Shimadzu, Model LC20AD, Japan". An infrared spectrum of the terpolymer was scanned using "Avatar spectrophotometer, Model 330, USA". The UV–vis spectrum of the terpolymer was recorded in "Shimadzu spectrophotometer, Model 1601PC, Japan". The $^{1}H$ NMR spectrum was recorded on a Bruker 400 MHz (USA) NMR spectrometer and $^{13}C$ NMR spectrum was recorded on a Bruker 100 MHz (USA) spectrometer. The morphology of the terpolymer was examined by SEM in Hitachi instrument (Model S-3000H, Japan) at 5400× and 15,000× magnifications. The XRD analysis was performed with Panalytical instrument (X'pert PRO Model, The Netherlands). The thermal stability of the terpolymer was observed by TGA using Thermogravimetric analyzer instrument (Model SDT Q600, USA) at a heating rate of 20 °C/min in static nitrogen atmosphere.

### 2.3. Ion-exchange properties

The ion-exchange properties of the synthesized chelating terpolymer were studied by batch equilibrium method [22]. The finely grounded terpolymers were used to determine their ion-exchange capacity for specific metal ions such as $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ in the form of their aqueous metal nitrate solutions rather chlorides or sulphates in order to avoid the precipitation of the chosen metal ions under varying experimental conditions. Chelation ion-exchange property of the terpolymer was studied with various electrolytes in different concentrations, pH ranges, and contact time intervals to substantiate the effectiveness of the terpolymer under changing experimental conditions as reported our earlier literature [10,12,14].

## 3. Results and discussion

BTF terpolymer was synthesized by the polycondensation of 2-amino-6-nitro-benzothiazole and thiosemicarbazide with formaldehyde (Scheme 1). It is more likely that removal of water molecule takes place by means of a condensation polymerization. The solubility behaviour of the terpolymer was analyzed with some common low polar, high polar and non-polar solvents (Table 1). It is observed that the synthesized resin is insoluble in benzene, xylene, toluene, and water. But, the resin is found to be soluble in dimethylformamide, tetrahydrofuran, dimethylsulphoxide, and partially in aqueous sodium and potassium hydroxide solutions.

### 3.1. Stability of the resin

The terpolymer resin are immersed in different solvents such as $HNO_3$ (2.0 mol/L), HCl (2.0 mol/L), acetone, ethanol, methanol, and benzene for 72 h, no monomers or other products are found to form in these solvents. This confirms that the chelating resins are highly stable in acidic, alkaline, and organic solutions. Generally,