



HEAVY METAL ABETMENT EFFICACY OF NEW IMPROVED SURFACE MODIFIED CO-POLYMER

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ABSTRACT

Selenium in its oxyanion form is major cause of contamination in mining aqueous waste streams. The aqueous oxyanions are rather more toxic than elemental form of selenium. Excessive intake of Selenium can cause dizziness, fatigue, irritations of the mucous membranes, collection of fluid in the lungs and bronchitis. Therefore, research is required to explore efficient methods for abatement of excessive toxic Selenium from contaminated water. In the present investigation, initially 4-HAOT-II co-polymer was synthesized in the laboratory and its structure has been assigned based on physico-chemical evidences. This co-polymer was subjected to surface modification employing molecular adsorption deposition method. This improved surface modified co-polymer has been characterized using modern techniques like FTIR, SEM and XRD. It was tested for selenium removal efficiency from contaminated water. The material reported in the present article has shown an excellent efficacy towards removal of excessive toxic oxyanion Selenium from contaminated water. Thus, it can be used successfully for wastewater treatment.

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INTRODUCTION

Heavy metal pollution in the aquatic system has become a serious threat today and of great environmental concern as they are non-biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soil and water. Selenium is a naturally occurring metalloid that belongs to the chalcogen group. Selenium is widely applied in global industries such as electronics, fertilizers, fungicides, antidandruff shampoos and many more. Amongst toxic substances reaching hazardous levels are heavy metals. (Regine and Volesky 2000) Heavy metals of concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. (Ahalya et al., 2003) Commercial quantities of selenium are generated during copper electrolytic refining. (USGS 2007; Lenz and Lens 2009) Selenium, in small quantities (0.1-0.5 ppm dry weight) is a micronutrient that is a part required in everyday life. Selenium becomes toxic at concentrations > 3 ppm dry weight. The National Primary Drinking Water Standard is 50 ppb for total selenium and the National Fresh Water Quality Standard is 5 ppb for total selenium. (EPA, 2011; EPA, 2001) The use of co-polymers in all spheres of life has been abundantly increased in recent years because of their novelty and versatility. They occupy the pivotal position in the

field of polymer science. The progress in this field has been extremely rapid, as they are generally useful in packaging, adhesives and coatings in electrical sensors, ion-exchangers, organometallic semiconductors, activators, catalysts and thermally stable materials etc. (Masram et al., 2010) Application of terpolymer (a special class of co-polymer) composite as an excellent adsorbent for removal of carcinogenic Cr (VI), a heavy metal, from polluted water has been reported in the literature. (Rahangdale et al., 2013) A new surface modified 4-HAOT-II (4-Hydroxyacetophenone-Oxamide-Trioxane- II) co-polymer sorbent was successfully synthesized by coating graphine oxide onto 4-HAOT-II co-polymer. The new surface modified improved sorbent was characterized by Fourier Transform Infra Red (FTIR), scanning electron microscopy(SEM) and X-Ray Diffraction (XRD) studies. The newly obtained surface modified copolymer have been proved to be a very good adsorbent which can be successfully used for removal of toxic oxyanion selenium from contaminated water which can then be used for safe potable purpose.

MATERIALS AND METHODS

Starting Materials

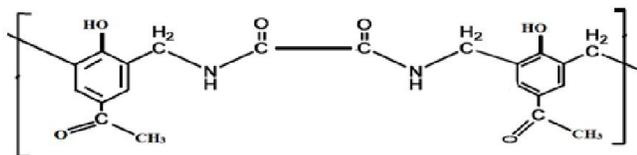
Few starting materials were self prepared in the laboratory and others were purchased from the market. 4-Hydroxy acetophenone (4-HA) was prepared in the laboratory starting

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from phenol by its acetylation followed by Fries migration reaction. The other starting materials like oxamide(O), trioxane (T) and graphine(G) etc. used in the synthesis of 4-HAOT-II copolymer were procured from reputed companies, like Merk, Mumbai, India and all were of analytical or chemically pure grade. The solvents like N,N-Dimethyl formamide (DMF) and Dimethyl sulphoxide (DMSO) were also of AR grade and were triple distilled under reduced pressure prior to their use in various physicochemical and spectral studies. Deionized (DI) water was used throughout the course of this investigation.

### Synthesis of 4-HAOT-II co-polymer

The 4-HAOT-II co-polymer was synthesized by condensing 4-Hydroxyacetophenone and oxamide with trioxane in the molar ratio 6:3:2. Hydrochloric acid (2M) was used as a catalyst. The reaction mixture was heated at  $382 \pm 2\text{K}$  in an electrically heated oil bath for about 5 hours. Voltage regulator and dimerstat was applied to maintain constant temperature of the bath. The solid mass obtained was immediately removed from the flask as soon as the reaction period is over. The separated polymeric mass having resinous texture was washed repeatedly with hot DI water and dried. The dried mass was washed with petroleum ether to remove unreacted starting materials or 4-HA-Trioxane copolymer formed, if any. The co-polymer was purified by dissolving it in 2.5N NaOH solution and reprecipitating it by dropwise addition of 1:1 (v/v) HCl/DI water. The purification by precipitation process was repeated twice. The resulting co-polymer sample was washed several times with boiling water, filtered and dried in vacuum at room temperature. The purified co-polymer was finally ground well to pass through a 300 mesh sieve and kept in vacuum over silica. The yield of co-polymer was found to be 80%. The purity of co-polymer was tested and confirmed by Thin Layer Chromatography (TLC) method. The proposed most possible structure of 4-HAOT-II copolymer is shown below:



Structure of 4-HAOT-II copolymer

### Surface Modification of 4-HAOT-II Copolymer

#### Preparation of 4-HAOT-II copolymer gel

50g of copolymer was slowly added to  $1\text{dm}^3$  of 10% by weight of oxalic acid with constant stirring. The mixture was heated to  $318 \pm 2\text{K}$  for proper mixing and then allowed to cool slowly. The pinkish viscous gel was obtained at room temperature.

#### Preparation of graphine oxide

Graphine oxide is prepared in the laboratory by known method and purified prior to its use. The finely powdered sample was passed through 150 mesh sieve to get its particles having uniform size. The blackish brown powder was stirred with 10% aqueous oxalic acid for 4h at room temperature. Graphine oxide was filtered from the acid, washed twice with DI water and again dried in oven at about  $333\text{K}$  over night.

### Preparation of surface modified copolymer

The 4-HAOT-II copolymer gel prepared as above was diluted two fold with DI water and heated to  $318 \pm 2\text{K}$ . 2.50 g of acid treated graphine oxide was slowly added to the diluted 4-HAOT-II copolymer gel and stirred for 24 h. The contents were allowed to settle and the clear liquid was filtered out under vacuum with Whatmann 41 filter paper. The surface modified copolymer, so obtained, was washed twice with conductivity (DI) water and dried in the oven at  $318\text{K}$  under vacuum for 24h. The coating process was repeated on the once coated sorbent for purpose of maximum loading of graphine oxide on the surface of 4 HAOT-II. The second coating process was completed within 20h. Similar procedure was employed for third coating too. Excess of oxalic acid in the sorbent was exactly neutralized by treatment with calculated quantity of standardized 2.5N aqueous NaOH. The mixture was then filtered with Whatman 41 filter paper, washed repeatedly with DI water and filtered. The thrice coated sorbent was dried in the oven under vacuum at  $318\text{K}$  for about 36 h and transferred to a glass bottle for storage in a desiccator.

### Characterization of surface modified copolymer

Characterization of surface modified co-polymer has been carried out employing the techniques like Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analysis and the concerned spectra/image have been presented in Fig.1,2 and 3.

## RESULTS AND DISCUSSION

### Characterization of surface modified 4-HAOT-II copolymer

FTIR spectrum of surface modified 4 HAOT-II copolymer is shown in Fig.1. The band at  $3445.27\text{cm}^{-1}$  indicates presence of the hydroxyl group stretching. The band at  $2662.41\text{cm}^{-1}$  is due to the C-H bond stretching of carbonyl group. The shifting of band from its standard value ( $2889.21\text{cm}^{-1}$ ) may be due to the involvement of graphin oxide during surface modification. The absorption at  $1633.30\text{cm}^{-1}$  is due to the C=O stretching mode. The two characteristic bands appeared at  $1005.85\text{cm}^{-1}$  and  $911.73\text{cm}^{-1}$  are indicative of the skeletal stretching vibrations. The peaks at  $532.07\text{cm}^{-1}$  and  $464.47\text{cm}^{-1}$  correspond to N-H bending.

SEM image of newly synthesized surface modified 4 HAOT-II copolymer has been presented in Fig.2. The SEM micrograph shows meso type structural surface morphology of surface modified 4- HAOT-II copolymer, which may depend upon its crystallinity. The photomicrographs of newly synthesized surface modified copolymer exhibited well-defined narrow shaped excellent crystal edges. A meso porous material is characterized by pores with diameter 2-50  $\mu\text{m}$ . It is evident from the SEM image that meso-structure of the material exhibits highly porous nature, which makes it an excellent host for sensing molecules/ions; since the species to be sensed get easily diffused towards the sensing center under such favorable situation.

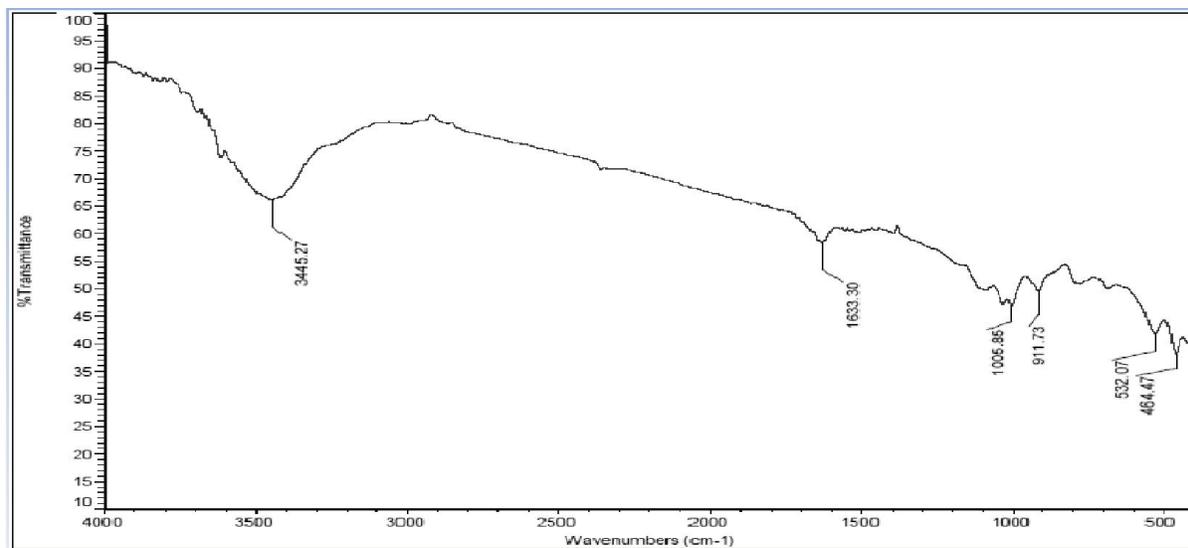


Fig.1. FTIR of surface modified 4 HAOT-II copolymer

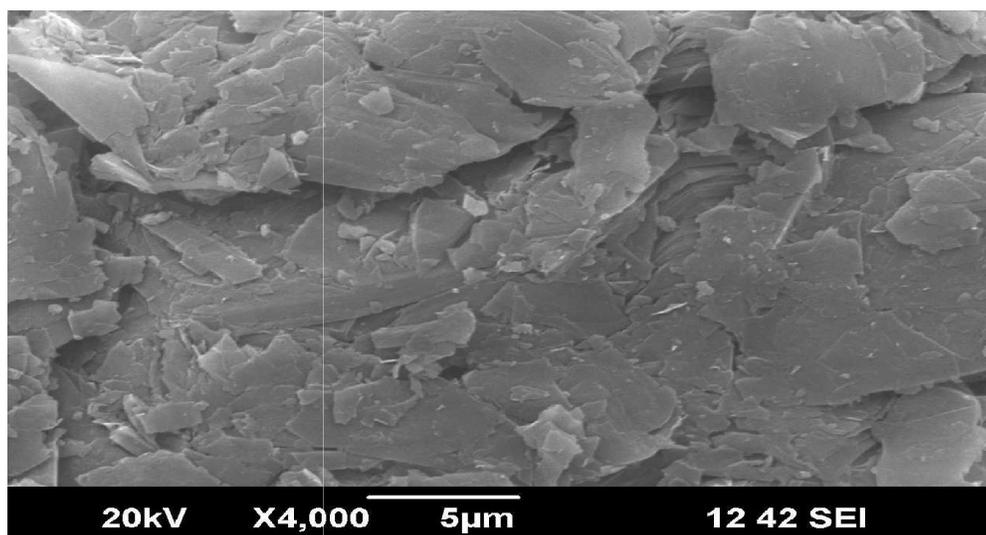


Fig.2. SEM image of modified 4 HAOT-II copolymer

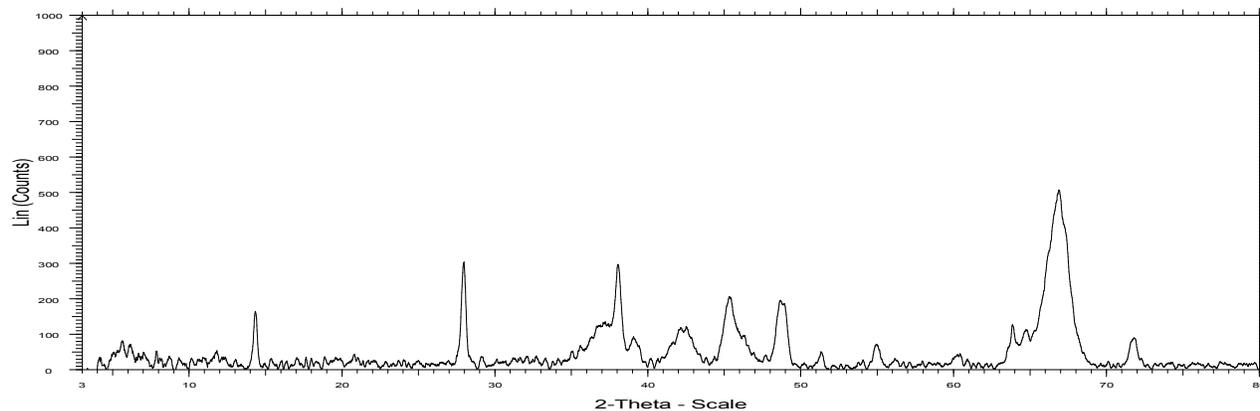


Fig 3. XRD pattern of surface modified 4 HAOT-II copolymer

Fig.3 represents X-ray diffractogram of surface modified 4-HAOT-II copolymer. The XRD spectrum of newly surface modified copolymer illustrates the presence of some minerals which might have incorporated along with graphine. The first peak at nearly  $2\theta = 65^\circ$  to  $67^\circ$  shows amorphous nature of the material while the peak at  $2\theta = 27^\circ$  to  $29^\circ$  shows material may be because of semi crystalline nature. The peak at  $2\theta = 65^\circ$  to  $67^\circ$  value, located graphine whose structure is tetragonal or ditetragonal. Thus, the material under study is composed of mixture of semi-crystalline and crystalline solid.

#### Removal of Oxyanion Selenium by surface modified 4-HAOT-II copolymer

Atomic Absorption Spectrophotometer (AAS) was used to determine Se concentration in aqueous solution before and after the treatment. The removal of oxyanion selenium by surface modified 4-HAOT-II as an adsorbent was carried out at the pH 6.00. The initial concentration taken was 25 mg/lit and adsorbent dose was 5.00 gm/lit. The results are given in Table 1.

**Table 1. Removal of selenium at pH = 6.00 and adsorbent dose 5.00 gm/lit with different contact time**

Contact Time(in min)	10	20	30	40	50	60	70	80	90
% of removal of Se	45	49	54	60	71	78	81	81	81

It can be noted that the removal of oxyanion selenium increased with increase in contact time. It is evident that 4-HAOT-II-GO material is effective for maximum removal of oxyanion selenium when the contact time was 70 min. No significant change in selenium removal efficacy was observed beyond 70 min. thus the optimum treatment time is 70 min.

#### Conclusion

- 4-HAOT –II copolymer is successfully synthesized with a good yield based on condensation reaction of 4-Hydroxy acetophenone and oxamide with trioxane in the molar ratio of 6:3:2 in the presence of HCl as a catalyst
- The surface modified 4- HAOT-II co-polymer adsorbent is also successfully prepared and characterized by FTIR, SEM and XRD studies.
- The surface modified copolymer is proved to be an excellent sorbent for Selenium because coating process has improved the uptake capacity of 4-HAOT-II copolymer selectively for Se and more active sites have been exposed on the modified improved sorbent.
- The newly developed surface modified 4-HAOT-II copolymer sorbent can be used to remove toxic selenium from industrial/mining effluents *i.e.* contaminated water. Thus, the water can be purified and used for potable purpose after treatment using this material.

- 25ml/lit. adsorbent dose, 6.00 pH and 70 min. treatment time are the optimum parameters for efficient application of the improved surface modified copolymer material under present investigation.
- Studies can be extended for testing applicability of this material for removal of other toxic heavy metals from contaminated water and fabrication of suitable columns for water purification using this new improved surface modified 4-HAOT-II copolymer adsorbent.

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