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HEAVY METALS REMOVAL BY THREE ARM STAR POLYMER BASED ON 2, 4, 6-TRIS HYDROXYMETHYL PHENOL AND POLYACRYLAMIDE

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ABSTRACT: Groundwater pollution by heavy metals, arising either from natural soil sources or from human activities, is a matter of extreme concern. In this article, contaminated water has been treated with three arm star polymers based on 2, 4, 6-tris hydroxymethyl phenol and polyacryamide. Five different grades of star polymers have been synthesized (THP-PAM1 to THP-PAM5), by free radical solution polymerization technique, by varying the amount of acrylamide. Further study of flocculation performance in kaolin suspension using jar test and settling test methods is reported. Among the five grades of star polymers, THP-PAM4 shows best flocculation performance. THP-PAM4 has been used to study the absorption of heavy metals (As, Cd and Hg) from contaminated water. The heavy metal absorptions have been analysed by AFM, FT-IR, EDAX, SEM, and TGA.

KEYWORDS: Star polymers; Flocculation; Heavy metals removal; Polyacrylamide; Polymer-metal complex

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1. INTRODUCTION

The free occurrence of heavy metals in the environment has been a major problem because of their toxicity and hazardous effect on human life and the environment [1, 2]. As a consequence of industrialization and urbanization [3], the presence of heavy metal ions in water streams has been promptly increasing since the last 50 years [4, 5]. Industrial wastewaters with dissolved toxic heavy metals such as arsenic, cadmium and mercury are reckoned to be non-biodegradable, and accumulated in humans and other living organisms; thus, ultimately inducing various diseases and malfunctioning [6-8]. Mercury, being non-biodegradable, has maximum permissible contaminant level of 2 ppb in drinking water. It is classified as a major pollutant by the United States Environmental Protection Agency (US-EPA) [9]. Highly toxic methyl mercury is prepared from mercury by certain biological processes in water and it accumulates in fish and its predators [10]. Mercury exposure can lead to alteration of the endocrine system, reduced fertility, slower growth, and development and abnormal behaviour that affects survival [11, 12]. Arsenic, a metalloid, is a poisonous crust element and exists as oxide or anion. It is known to be the 20th most abundant element in the earth [13]. Arsenic abundance in water is due to biological activity, combustion of fossil fuels, geochemical reactions, gold mining, natural weathering process, volcanic eruptions, leaching of man-made arsenic compounds, smelting of metal sores, desiccants, wood preservatives, agricultural pesticides and many other anthropogenic activities [14, 15]. Arsenic is broadly present as both arsenic (V) and (III), depending on pH and redox conditions [16, 17]. Arsenic (III) is deadlier than arsenic (V), because arsenic (III) has higher affinity to bind with variety of proteins containing vicinal sulfhydryl groups and inhibits their activity. Long term consumption of arsenic contaminated drinking water induces skin, lungs and kidney cancer, gastrointestinal disease, bone marrow disorder, cardiovascular diseases and other diseases. Due to tremendous toxicity of arsenic in drinking water, World Health Organization (WHO, Geneva, Switzerland), Environmental Protection Agency (US-EPA, United States) and Central Pollution Control Board (CPCB, India) have set 0.01mgL^{-1} to 0.05 mgL^{-1} as maximum permissible limit of arsenic in drinking water (IARC, 2013) [18]. Cadmium is less abundant on earth, exist in water as a hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulfates, or as organic complexes with humic acids. Cadmium retrieved in groundwater is due to weathering and erosion of soils, atmospheric deposition, direct disposal from industrial effluents, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Cadmium toxicity cause renal disturbances, lung problems, bone lesions, cancer and hypertension in humans [19-21] Thus, the removal of these toxic metals from wastewater is a crucial issue. Many conventional processes like adsorption, coagulation, co-precipitation, ion-exchange and oxidation-reduction process have been reported in literature for treatment of arsenic and removal of heavy metals from wastewater [22-29]. Among these processes, absorption is one of the promising methods. The aim of this work is to synthesize environment friendly polymeric materials in laboratory scale and to study in detail the process of removal of arsenic (III), cadmium (II) and mercury (II) from water by using these materials.

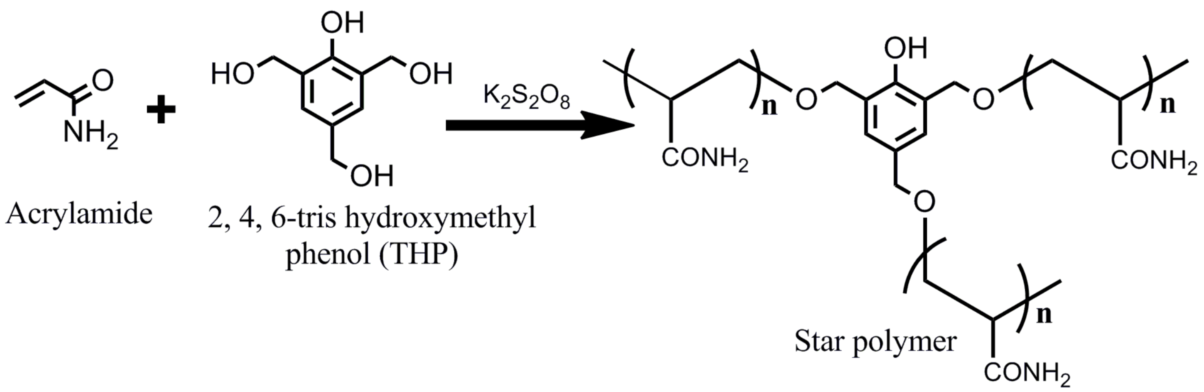
2. MATERIALS AND METHODS

Materials

Cadmium nitrate and arsenic trioxide were procured by S D Fine-Chem. Ltd, Maharashtra, India. Mercury (II) chloride was procured by Sigma Aldrich, India. Acetone was supplied by Spectrochem, Mumbai, India.

Synthesis of three arm star polymers

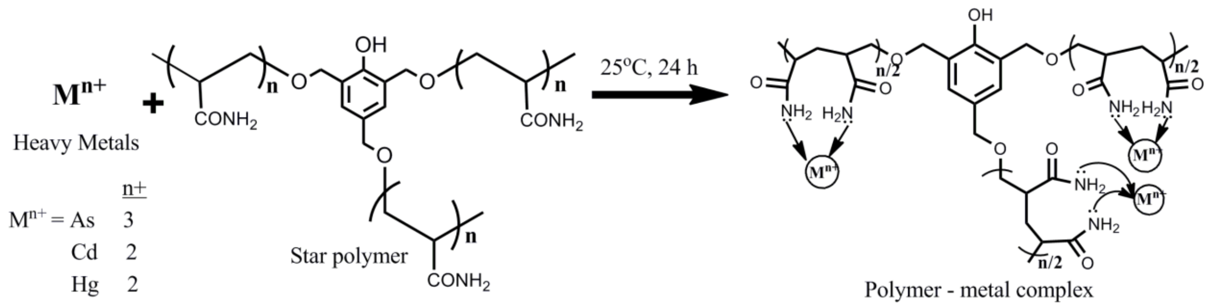
Star polymers were synthesized by free radical solution polymerisation technique using potassium persulphate as an initiator. Star polymers were fabricated by 2, 4, 6-tris hydroxymethyl phenol as a central moiety with three polyacrylamide chains as three arms. Five different grades of star polymers (THP-PAM 1 to THP-PAM 5) were synthesized by varying the amount of acrylamide. The polymerisation reaction is shown in **Scheme 1**. The synthesis procedure and characterisation of all grades of star polymers are given in details at Kumar et. al. [30].



Scheme 1 Synthesis of three arm star polymer by free radical polymerization.

Heavy metal removal

Heavy metals get absorbed into star polymers by simply blending star polymers with heavy metals in ratio 10:1. For this, 500 mg of star polymer and 50 mg mercury (II) chloride were dissolved in 20 mL and 5 mL of water respectively. The two solutions were mixed together and stirred for 24 h at room temperature. The mixture is precipitated in acetone followed by three times washing for removing dissimilated heavy metal from polymer-metal complexes. Synthesis of polymer-metal complexes is shown in **Scheme 2**. Then it is dried in vacuum oven over 15 mm of Hg at 40ºC, till constant weight and grinded to powder. For other heavy metals like arsenic and cadmium absorption the above procedure is followed. However, in case of arsenic absorption, the arsenic metal solution was prepared at 70ºC.



Scheme 2 Synthesis of polymer metal hybrids.

Characterization

Spectrophotometer Thermo Nicolet FT-IR (Model Jasco FT-IR 5300) was used to record FTIR spectra of THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg within the range of 4000-400 cm^{-1} by using solid state KBr pellet method. FT-IR spectrum is shown in **Figure 1**. HRSEM SUPRA 40, ZEISS (Germany) was used for the SEM study and THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg were used in the form of powder. SEM images are shown in **Figure 2**. DTG analysis of THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg were recorded by TGA-DTA (Perkin Elmer STA 6000, USA). DTG analysis of the sample was carried out from 50ºC to 600ºC, under inert atmosphere (N_2 gas). The heating rate was 10ºC/min. The DTG plots are shown in **Figure 3**. HRSEM SUPRA 40, ZEISS (Germany) was used for EDAX analysis. EDAX instrument had been connected to SEM (HRSEM SUPRA 40, ZEISS) instrument. THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg were used in the form of powder. EDAX spectrums and elemental quantitative analysis are shown in **Figure 4** and **Table 1**, respectively. AFM images were recorded by NT-MDT Model Solver NEXT. Roughness and peak height were reckoned by a software NOVA Px 3.1.0 Rev 3880 which was furnished by the manufacturer. The images were recorded in a semicontact mode by using a noncontact silicon cantilever (NSG10-DLC). THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg films were fabricated by dissolving 10 mg polymer sample in 100 µL water to form clear solution and 20 µL of this solution was dumped on glass slide of approximate size (1 cm x1 cm), allowing for air dry. Air dried followed by vacuum dry for 24 h before AFM observation. The roughness was determined with the root-mean-square (RMS) and average roughness of 10 x 10 µm scan areas of the respective materials. AFM three dimensional images of THP-PAM4, THP-PAM4-Hg, THP-PAM4-Cd and THP-PAM4-As is shown in **Figure 5**.

3. RESULTS AND DISCUSSION

Synthesis of star polymer

Five grades of star polymers were synthesized by varying the amount of acrylamide and keeping other reaction parameters constant. Among the all grades THP-PAM4 had longer polymer chain length and higher molecular weight as observed by intrinsic viscosity measurement and GPC analyses (Kumar et al., 2014).

Heavy metal removal

Polyacrylamide contains amide functionality which has two donor sites viz., oxygen of carbonyl group and nitrogen of –NH_2 group. Heavy metals form complexes between polyacrylamide donor sites by co-ordination bonds and adhere with polymers. Because of its higher molecular weight and longer polyacrylamide chains, THP-PAM4 has maximum probability of interaction with heavy metals. Thus, it has been chosen for heavy metal absorption study.

Characterization

FT-IR

Complex formation between heavy metals and amide groups of polyacrylamide chains in the star polymers leads to shifts in N-H asymmetric and symmetric stretching frequencies shifted towards lower region, -C=O stretching frequency of amide group shifted towards higher region and N-H bending of amide shifts towards lower region. In IR spectrum of THP-PAM4, -C=O stretching frequency and N-H bending of amide were observed at 1654 cm^{-1} and 1611 cm^{-1} respectively. Apart from these bands, C-H stretching at 2928 cm^{-1} was also observed. The broad band at 3447 cm^{-1} was attributed to the combination of O-H stretching of phenol, asymmetric and symmetric N-H stretching frequency of amide. In the case of complexes THP-PAM4-Hg, THP-PAM4-Cd and THP-PAM4-As the -C=O stretching frequency shifted from 1654 cm^{-1} to 1657 cm^{-1}, 1662 cm^{-1} and 1663 cm^{-1} respectively, i.e., towards the higher region. In THP-PAM4-Hg, THP-PAM4-Cd and THP-PAM4-As N-H bending stretching shifted towards lower region, i.e., from 1611 cm^{-1} to 1602 cm^{-1}, 1608 cm^{-1} and 1603 cm^{-1} respectively and also N-H asymmetric and symmetric stretching frequency of amide shifted, to lower region, from 3447 cm^{-1} to 3420 cm^{-1}, 3426 cm^{-1} and 3423 cm^{-1} respectively.

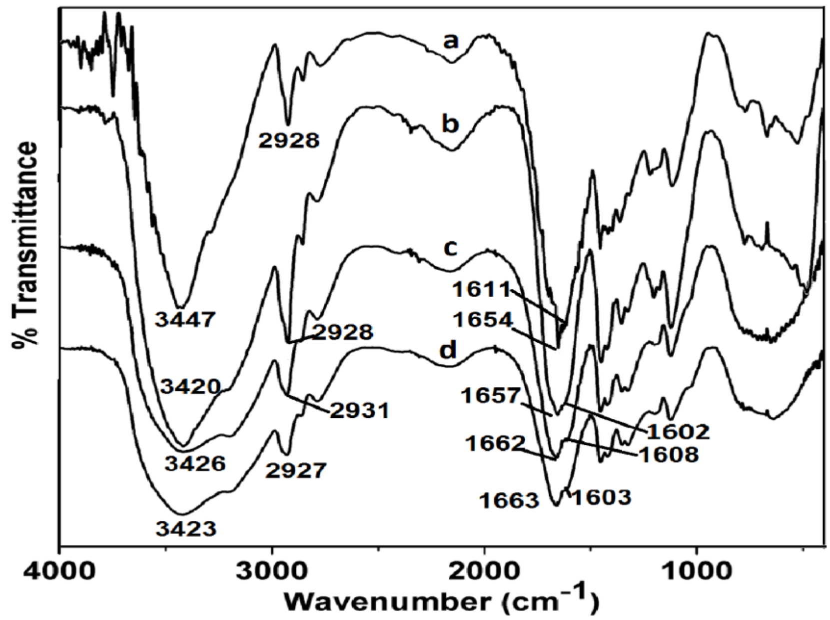


Figure 1 FT-IR spectrum of (a) THP-PAM4, (b) THP-PAM4-Hg, (c) THP-PAM4-Cd and (d) THP-PAM4-As.

SEM analysis

Figure 2 a, 2 b, 2 c, and **2 d** show the SEM images of THP-PAM4, THP-PAM4-As, THP-PAM4-Cd and THP-PAM4-Hg, respectively. **Figure 2 a** showed that the surface morphology of THP-PAM4 was porous in nature and other three images **Figure 2 (b, c, and d)** showed the surfaces are rough. After metal absorption, the porous surface of star polymer transformed into rough surface. Thus, it was evident that heavy metals had been absorbed on polymer surface.

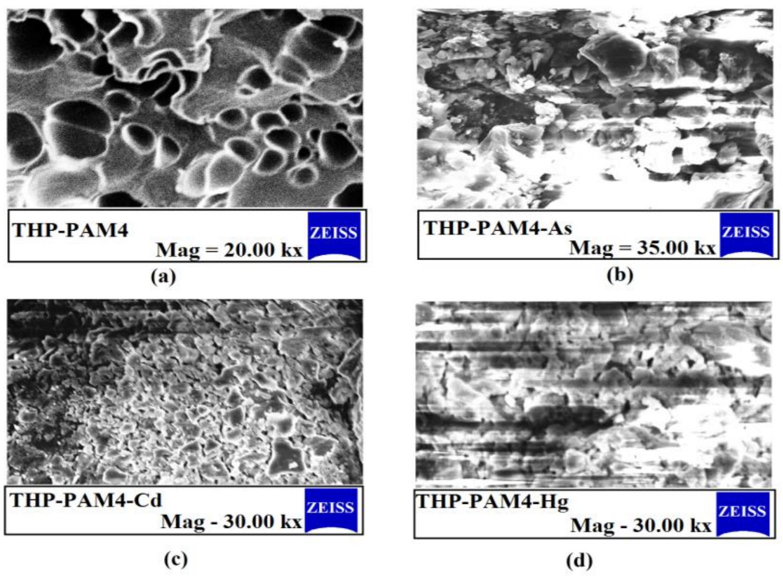


Figure 2 SEM images of (a) THP-PAM4 (b) THP-PAM4-As (c) THP-PAM4-Cd and (d) THP-PAM4-Hg.

Thermal analysis

In TGA analysis, THP-PAM4 showed first weight loss at 101°C due to loss of absorbed moisture in the sample. Second weight loss at 210°C was due to the breakage of ether bond. The third weight loss observed at 282°C corresponded to the loss of ammonia from the side chains of polymers and further loss at 359°C corresponded to the degradation of polymers. In thermal analysis of heavy metal-polymer complexes, the weight loss patterns are same but the % of weight loss is different. Degradation is dependent upon the interaction between metal and polyacrylamide chains. Among the star polymers and three metal-polymer complexes, THP-PAM4-Cd and THP-PAM4-Hg are thermally more stable than THP-PAM4 and THP-PAM4-As is the least stable complex. Thus THP-PAM4-metal complexes constituted more stable complexes with M (II) than M (III).

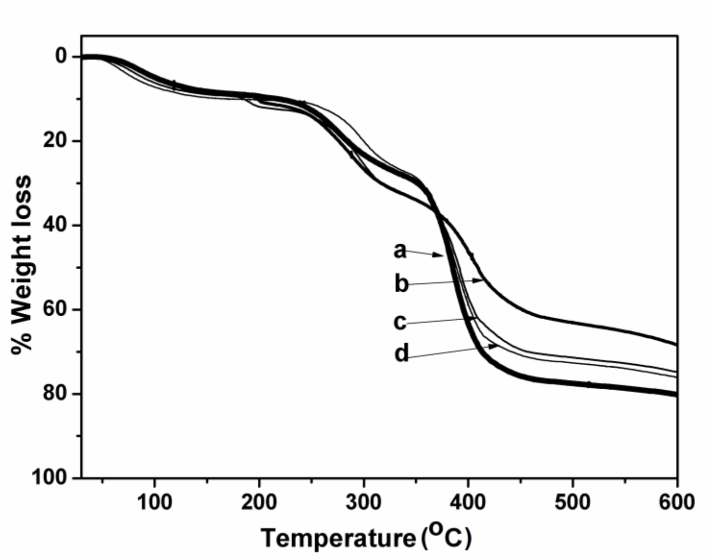


Figure 3 Thermal analysis of (a) THP-PAM4-As (b) THP-PAM4-Cd (c) THP-PAM4-Hg and (d) THP-PAM4.

EDAX analysis

Table 1 EDAX quantitative analysis results of THP-PAM4, THP-PAM4-As, THP-PAM4-Cd, and THP-PAM4-Hg.

Serial no.	Element	THP-PAM4		THP-PAM4-As		THP-PAM4-Cd		THP-PAM4-Hg	
		Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
1	C	90.01	74.31	40.57	60.72	183.28	48.63	183.70	56.03
2	O	41.23	25.55	30.29	34.04	231.36	46.09	173.11	39.64
3	Mg					24.76	3.25	12.98	1.96
4	Cl							5.51	0.57
5	Ca			9.48	4.25	24.45	1.94	12.66	1.16
6	Hg							35.36	0.65
7	Au	2.70	0.14						
8	As			4.09	0.98				
9	Cd					3.01	0.09		
	Total	133.94		84.43		466.86		423.33	

In EDAX analysis, THP-PAM4 only showed the peaks for C, O and Au. THP-PAM4-Hg showed the peaks for C, O, Hg and Ca. THP-PAM4-Cd showed the peaks for Cd, Ca, Mg and C and THP-PAM4-As showed the peaks for As, Ca, C and O.EDAX analysis, is a qualitative analysis, and proved that THP-PAM4 removed heavy metal from aqueous solution. During EDAX analysis, elemental analysis was performed at selected region of sample (polymer and polymer-metal complex). It was evident that THP-PAM4 was more efficient to bind with mercury (II) upto 35.36 % weight. THP-PAM4-Cd contained 3.01 % weight of Cd and THP-PAM4-As contained 4.09 % weight of As.

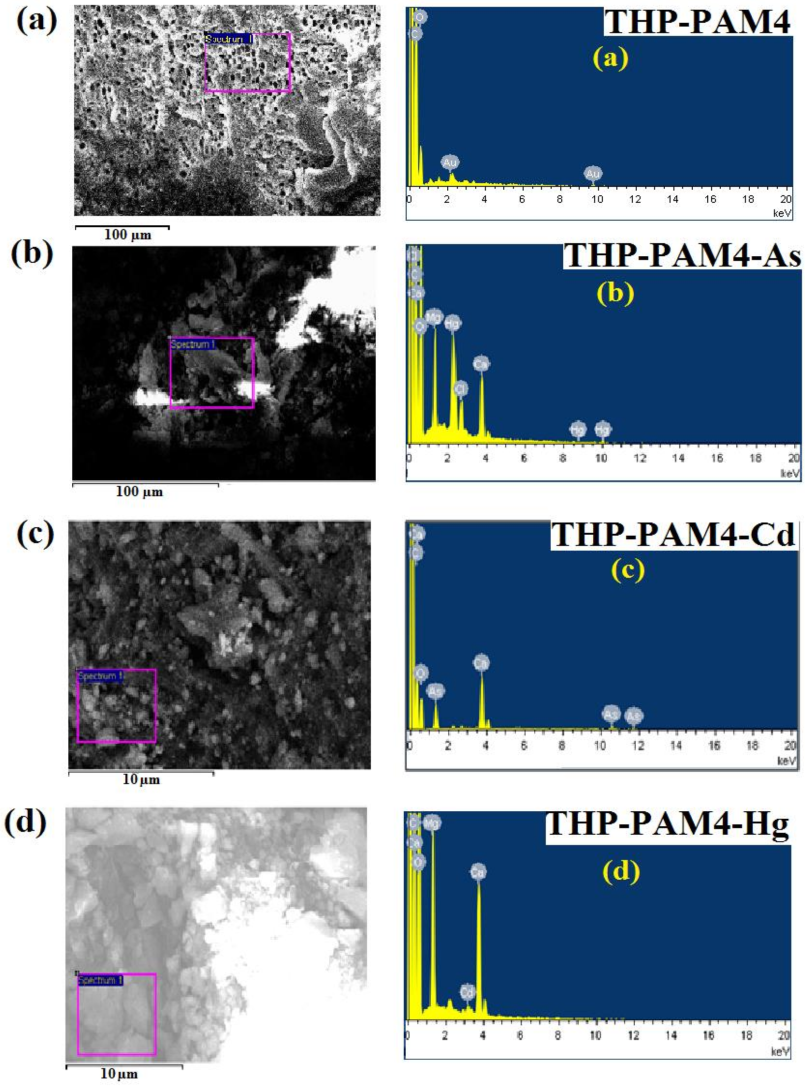


Figure 4 EDAX analysis (Elemental spectra) of (a) THP-PAM4 (b) THP-PAM4-Hg (c) THP-PAM4-As and (d) THP-PAM4-Cd.

AFM analysis

The three dimensional AFM images showed the nature of phase-separated structures and surface morphology. AFM provided concurrent detection of phase and surface roughness. The phase-separated morphologies of polymer and all polymer-metal complexes are shown in **Figure 5**. The surface root mean square and average roughness, of THP-PAM4 was 0.257 nm and 0.202 nm, of THP-PAM4-Hg was 0.966 nm and 0.626 nm, of THP-PAM4-Cd was 0.617 nm and 0.464 nm and of THP-PAM4-As was 0.780 nm and 0.302 nm respectively. Among all the complexes, THP-PAM4-Hg showed highest surface roughness. AFM analysis also supported the SEM results. Thus, heavy metal was absorbed on polymer. From the AFM analysis of the polymer and polymer-metal complex, visual evidence for the appearance of phase separated structures was observed.

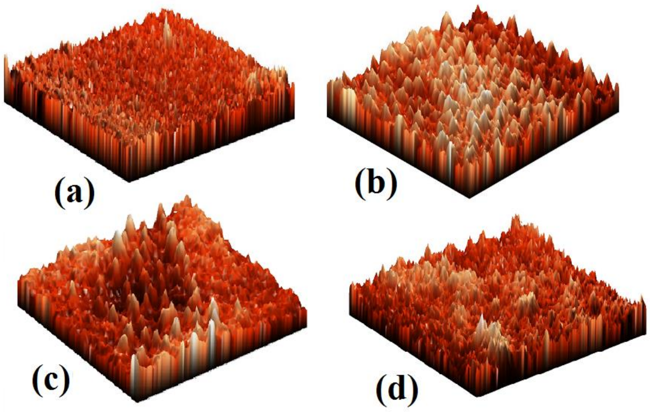


Figure 5 AFM three dimensional image of (a) THP-PAM4 (b) THP-PAM4-Hg (c) THP-PAM4-Cd and (d) THP-PAM4-As.

4. CONCLUSIONS

Among the five grades of star polymers synthesized, THP-PAM4 was chosen for removal of heavy metal from aqueous solution. The metal absorption by star polymer was proved by AFM, EDAX, FTIR, SEM and thermal analysis. Increase in surface roughness of metal complexes observed by AFM analysis proved heavy metal absorption by THP-PAM4. Among other heavy metals, Mercury efficiently binds with star polymer. FTIR analysis showed that shifts in NH stretching and N-H bending of amides towards lower region and -C=O stretching towards higher region thereby proving complex formation between heavy metals and amide group of polyacrylamide chains in the star polymer. SEM analysis showed that the surface morphology of THP-PAM4 was porous in nature. On metal absorption, the porosity of the complexes reduced drastically. Among the star polymer and metal-polymer complexes, THP-PAM4-Cd and THP-PAM4-Hg were thermally more stable than THP-PAM4 and THP-PAM4-As. From this study, it was observed that THP-PAM4 was efficient in heavy metal removal from aqueous solution. Thus, these star polymers proved to be smart materials available for heavy metal removal from waste water.

CONFLICT OF INTEREST

The authors have no conflict of interest.

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