Research Article

Microwave-Assisted Synthesis And Characterization Of Eco-Friendly Composite SCBF-g-Poly (HEMA-co- AM)/MMT

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For developing agrowaste and green polymeric materials as superabsorbent, graft copolymerization of 2-hydroxyethyl mathacrylate (HEMA) and acrylamide (AM) with sugarcane bagasse fibre (SCBF) was carried out in presence of ammonium persulfate (APS) as initiator and N, N'- methylenebisacryamide (MBA) as crosslinker using copper sulfate and glycine as complexing agent in a microwave oven. Montmorillonite (MMT) clay was added with a view to synthesize green composite to enhance the water absorption capacity. The synthesized graft copolymer and composite were characterized by FT-IR, TGA, scanning electron microscopy (SEM). Observations reveal that the montmorillonite layers were exfoliated during polymerization process. Their water absorbing capacity and biodegradation under sludge water, soil burial method and cultured microorganism media were investigated for future application and commercial purposes. Also, adsorption of Fe²⁺, Cu²⁺ and Cr⁶⁺ ions on graft copolymers were studied for using in separation technologies. Water absorption capacity of composite is more than that of grafted copolymer and modified SCBF which can be used as conditioner with fertilizer and making green vegetation in the realm of dried land.
INTRODUCTION:

Inborn qualities like lignocelluloses, renewable and biodegradability of natural fibres, these are used in the world of composite. These fibres have gone one step ahead due to their eco-friendly nature and become substitute for synthetic fibres which are non-biodegradable and pollution creating agent. Therefore, agro-based waste products have been utilized as natural sources for structural components or fillers or reinforcing materials in the composite formation which offers wide spectrum of applications such as automotive interior components, aerospace applications, railway, military applications, buildings and construction industries, packaging consumer products where high performance and low cost have to be combined. The most important fibrous byproduct sugarcane bagasse fibre (SCBF) is obtained by extraction of juice from sugarcane bagasse which is disposed in various ways from which burning is one of the disposal method which releases air pollutants. India is one of the largest sugarcane bagasse producers in the world an estimated production of around 300 million tons per annum. Presently around 500 sugar factories are present in the country along with 300 molasses based alcohol distilleries [1].

Environment receives toxic heavy metals like iron, nickel, chromium, arsenic, cadmium, lead, zinc, copper, mercury, etc [2] due to growing industrialization, urbanization, and modern methods of agricultural and domestic activities. These toxic metals are non-biodegradable and accumulate in living organisms through food chain which are responsible for many health ailments and disorders [3]. Some heavy metals are essential for the metabolic processes, but their high concentration becomes toxic [4]. The acceptable limit of total chromium for drinking water is 0.1 mg/L as per US, EPA standard (Environmental Protection Agency EPA). Both Cr$^{3+}$, Cr$^{6+}$ are dangerous, but hexavalent chromium has greater risk due to its carcinogenic nature [5]. Similarly, iron is an essential metal ion for human. Its standard concentration is 0.3mg/L (US EPA, 2012), but higher concentration causes diabetes, hypertension, etc. [6], [7].

Toxicity of Cu (II) for human beings is at levels of 100-500mg per day [8],[9]. According to WHO (The World Health Organization) guidelines the maximum acceptable concentration of copper in drinking water is 1.5mg/L. Copper toxicity causes itching and dermatization, keratinication of the hands and sole of feet in human beings [10], [11]. Intake of water having high concentration of copper causes gastro-intestinal irritation and possible changes in the liver and kidney [12]. Workers of various copper related industries are affected by lung cancer also. Therefore, it is extremely important and deserves immediate attention to remove heavy metals like Cu (II), Cr (VI), Fe (III) from waste water before discharge into aquatic system because water is elixir of life. Now-a-days, scientists have given more attention for preparing adsorbents from various waste materials generated by forestry [13], industry, fishery [14] and also agro-wastes [15]. In the present study, SCBF-g-Poly (HEMA-co-AM)/MMT composites were synthesized via free radical polymerization by microwave irradiation method. These are characterized by FTIR, TGA, and SEM. The grafted copolymer and composite synthesized were characterized putting special attention on their metal ion sorption, surface morphology, water absorption, and biodegradability for the futuristic application as an important biodegradable agro-waste.
was a waste residue of the sugarcane milling process obtained from traditional sugar juice maker around the Bhubaneswar and Cuttack town of Odisha State, India.

**Modification of SCBF**

The raw material obtained from juice maker was sun-dried for four days and the samples had moisture content of about 10g/100g. Initially, the dried bagasse was cut into 3-4 cm length. It was immersed in 1:1 benzene and methanol solution for 12 h to remove waxes and resins. Then it was washed with distilled water for three times and air dried till a constant mass was obtained. The dried materials were bleached with sodium hypochlorite (3%) solution for 24 h to remove the lignin content. Then, it was washed with double distilled water three times and dried in vacuum-evaporated oven at 50°C for 24 h. The bleached fibre was then reduced in size by a blender and screened with a sieve of mesh size number200. The modified material was stored in a plastic bag for synthesizing copolymer and composite.

**SYNTHESIS OF SCBF-G-POLY (HEMA-co-AM)**

The polymerization experiments were carried out in a whirlpool T120 microwave oven. The electromagnetic energy was produced by a magnetron at 2.45 GHz; the power could be adjusted between 0 to 700W continuously. The temperature of the reaction system was monitored with an IR temperature pickup with an internal cooling flask. The temperature could be adjusted precisely and independently of the microwave power. The mixed solution of the AM, HEMA and APS is mixed with 1g of modified SCBF and required amount of water is added to it with copper and glycine solution. The solution was bubbled with nitrogen for 1h to remove dissolved oxygen that would-be inhibitor for the reaction. Then the mixture was irradiated in microwave oven at 300W for 10 min. Heating was stopped and ice was added to stop the reaction then filtered and dried at 50°C for 24h. The copolymer formed was immersed in pure hot water for one day to eliminate non-reactive materials as well

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**EXPERIMENTAL PROCEDURE**

**Materials**

HEMA (Merck, Darmstadt, Germany), APS and MBA were purchased from Fluka (Buchs, Switzerland). Methanol, benzene and cobalt (II) chloride were from E.Merck, India. MMT clay with cation exchange capacity of 90 mequiv/100g was from Himedia and was used without further purification. All other chemicals were also of analytical grade. Milli-Q grade deionised water was used for preparing the solution. HEMA was vacuum distilled at 50°C/50 mm Hg prior to use in order to remove the inhibitor. In HEMA vacuum distillation, hydroquinone was added to prevent polymerization. The sugarcane bagasse fibre

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**Scheme 1 Formation of green composite**

SCBF-g-Poly (HEMA-co-AM)/MMT

**Scheme 2 Formation of Copolymer Poly (HEMA-co-AM)**
as homo polymers and copolymer poly (HEMA-co-AM) shown in scheme- 2 if any. Then it was filtered and dried under mixture was heated with microwave oven for 10 min. The reaction vessel was removed and kept in the ice bath for one h to stop the polymerization reaction. The composite formed was dissolved in hot water and then methanol solution for 24 h to remove homopolymer (PAM and PHEMA) and unreacted substances if any. The product was filtered and washed with deionised water. It was dried in oven at 50°C till a fixed weight of grafted composite SCBF-g-Poly (HEMA-co-AM)/MMT was obtained. It was kept in desiccator for characterization. It is shown in scheme 1.

CHARACTERIZATION
FT-IR Spectroscopy
The FT-IR spectra were used to analyze composition of the samples that gave information about grafting behavior and functional groups present in the composite structure in the vacuum at 30°C for 24 h. The dried range of 400- 4000 cm by a Perkin Elmer copolymer was stored in a clean dried container for characterization.

Synthesis of SCBF-g-Poly (HEMA-co-AM)/MMT Composite
Synthesis of composite was done in the above described Whilpool T120 microwave oven and all the conditions were similar as described. The experiments were carried out in two steps. In the first step 0.1g of modified SCBF and different proportion of AM, HEMA and initiator APS were taken in the reaction vessels and N2 gas was bubbled for 45 min to remove dissolved oxygen. Then the reaction vessels were stirred at 600 rpm at room temperature (28 °C) for 30 minutes to make it homogeneous. In the second step, requisite amount of CuSO4, glycine, MBA and 1% w/v MMT solution were added to the reaction mixture carefully. N2 gas was passed again for 10 min. The reaction Paragon 500 FTIR (Boston, MA) spectrophotometer using KBr pellets to prepare the samples.

Thermo Gravimetric Analysis (TGA)
Thermo gravimetric analysis (TGA) of the samples was carried out using a Shimadzu DTG-50 thermal analyzer. The samples were heated to a temperature of 500°C at a rate of 10°C/min starting from room temperature (28°C) under nitrogen atmosphere.

Scanning electron microscopy (SEM)
The morphological characteristics of modified SCBF, copolymer, and composite were observed by using a scanning electron microscope (Hitachi S4800, Japan).

PROPERTY STUDY
Metal Ion Sorption Studies
The synthesized copolymer absorbed Cu2+, Fe2+, and Cr6+ ions from their aqueous solutions and was analyzed for concentration of the rejected ions on a DR 2010 Spectrophotometer (Hach Co., USA) by using its standard pillow reagents that have high sensitivity with maximum limits of 5.0, 3.0 and 0.6 mg/L respectively of Cu2+, Fe2+, Cr6+ ions. All weights were taken on a Denver TK- 230 balance having a minimum readability of 1.0 mg. Ion sorption studies of SCBF, grafted copolymer and composites were carried by immersion of the sample for 3 h in 20 ml solutions of metal ions of known concentration. The pH of the solution was raised to 7.0 by using buffer solution. Metal ion uptake is expressed as Percentage of Metal ion Uptake (Pu) = (Amount of metal ions adsorbed)/ (Total amount of metal ions present) × 100

Water absorbency
1g of the sample was immersed in water at room temperature until equilibrium was reached. The water absorption was determined by weighing the swollen sample after it had been allowed to drain on a sieve for 10 min. The water absorbency [16] %Q was calculated using the following equation:

\[ %Q = \frac{(m - m_0)}{m_0} \times 100 \]

Where m and m0 denote weight of the sample swollen by water and weight of the absorbent respectively.
**Biodegradation**

Biodegradation of the samples were studied on two different methods mentioned as follows:

**Degradation by sludge water**

The activated sludge water was collected from septic tank receiving toilet and domestic waste water. The sludge water was collected in a polypropylene container, which was filled completely and then closed perfectly. Then the waste water was transferred to the lab immediately. After settling for 1h the total solid concentration was increased to 5000 mg/l. Then activated sludge water and sample (0.2g) were incubated together in a sterilized vessel at room temperature (28 ± 2°C). Duplicate samples were removed at time intervals for biodegradation study through weight loss. Vessels containing polymer sample without sludge water were treated as control.

**Soil burial degradation**

Biodegradability [17] of the samples in soil was studied by weight loss. Samples of 30 × 30 × 1 mm were weighed and then buried in boxes containing alluvial soil, collected from farmland topsoil before planting. Samples were buried at a depth of 20 cm. A controlled box containing only sample without soil was also taken as control. The burial samples were dug in certain time intervals, washed with distilled water, dried in a vacuum oven at 40°C for 24h, equilibrated in a desiccator for at least 24h and evaluated by measuring their dry weight.

**RESULT AND DISCUSSION**

**IR Spectra**

Lignin [18] in SCBF decreases the amount of grafting onto the back bone of the fibre. We, therefore, have taken lignin free SCBF whose IR-spectroscopy as shown in fig-1. The FTIR spectra of PAM have peaks at 3365.73, 1654.55, 1451.21, 1325.4, 634.3 cm⁻¹ and for modified SCBF peaks are at 3410, 2939.4, 1096.97, 897.9 cm⁻¹. In SCBF-g-poly (HEMA-co-AM) copolymer and SCBF-g-poly (HEMA-co-AM)/MMT composite, peaks found at 3401, 1649 cm⁻¹ indicate the N-H stretching and >C=O stretching of the amide bands respectively which are characteristics of the –CONH₂ group in the acrylamide. Also peaks for the –C-N stretching and the weak band for –N-H out of plane bending are obtained at 1390 and 599 cm⁻¹ respectively. A prominent peak at 1735 cm⁻¹ due to >C=O stretching of HEMA, that poly HEMA was incorporated on the cellulose backbone which was further confirmed by SEM micrograph (Fig 3) and also greater swelling ratio of copolymer and composite. Presence of MMT in the composite is confirmed by twin new peaks at 517 and 514 cm⁻¹ respectively due to the Al-O stretching and Si-O bending of MMT. Similar results were reported in the literature [19]. This is also confirmed by SEM micrograph (Fig 3) and large increase in water absorption ratio of the synthesized composite.

**TGA**

From the thermogram (TGA) curves as shown in Fig 2, it is found that the first weight loss at 65 to 78°C was due to the free water evaporation from PAM. The second weight loss at the temperature 275 to 290°C was due to the removal of SCBF from poly (HEMA-co-AM). The third weight loss around 340°C might be due to the decomposition of modified SCBF. The fourth weight loss around 405 to 425°C and 495 to 510°C might account for the complete degradation of SCBF, PHEMA, PAM and MMT from the synthesized composite. So comparing the thermogram (TGA) curves of PAM, modified SCBF, PHEMA, SCBF-g-Poly (HEMA-co-AM) copolymer and SCBF-g-Poly (HEMA-co-AM)/MMT composite, it was found that the temperature of decomposition (TD) is very much influenced by the addition of MMT. TD values and residual mass indicate that on addition of MMT the composite becomes more resistant to thermal action.
**Fig 1** FTIR spectra of (a) Modified SCBF, (b) PHEMA, (c) PAM, (d) Copolymer SCBF-g-Poly(HEMA-co-AM), (e) Composite SCBF-g-Poly(HEMA-co-AM)/MMT

**Fig 2** TGA thermograms of (a) PAM, (b) Modified SCBF, (c) PHEMA, (d) Copolymer SCBF-g-Poly(HEMA-co-PAM), (e) Composite SCBF-g-Poly(HEMA-co-PAM)/MMT

**SEM**

Scanning electron micrographs (SEM) of modified SCBF, copolymer SCBF-g-Poly (HEMA-co-AM) and composite SCBF-g-Poly (HEMA-co-AM)/MMT are shown in Fig 3. Figure 3(a) is associated with modified SCBF and upon its grafting with HEMA-co-PAM the surface morphology is changed as shown in Fig- 3(b). The penetration of the copolymer in lumens is seen as the white interior and also on the surface of the modified SCBF. It also appears that grafting of AM and HEMA led to physical and chemical crosslinking as well-defined pores are visible in these micrographs. The presence of MMT is clearly visible which is embedded onto the surface of the grafted copolymer SCBF-g-Poly(HEMA-co-AM) to form the composite Fig-3(c). On the addition of MMT to the grafted copolymer, the porosity of the composite increases to maximum which creates more place to carry more water than the grafted copolymer. This is confirmed by the more water absorbency of the composite as shown in Fig 5.
Metal ion sorption

It is found that the sorption by modified SCBF is more for Cr$^{6+}$ ions and second highest for Fe$^{3+}$ ions and least for Cu$^{2+}$ ions. It is perhaps due to the decrease of size of the ions and also decreases in oxidation state of the ions. Sorption of Iron ion is more than that of chromium ion which is more than that of copper ion in case of the copolymer. It is due to the presence of –CONH$_2$ groups along with ester moiety of the graft copolymer. Similar results are obtained in the literature [20]. Slight
increase in sorption of these ions by the synthesized composite than that of the copolymer. Perhaps it is due to formation of complex structure between the metal ions and oxygen atom of Al – O linkage and Si – O linkage of MMT. The result is shown in fig 4.

**Fig 4** Metal ion sorption of Cu$^{2+}$ ions, Cr$^{6+}$ ions and Fe$^{3+}$ ions by Modified SCBF, copolymer SCBF-g-Poly(HEMA-co-AM) and composite SCBF-g-Poly(HEMA-co-AM)/MMT

**Water absorbency**

Water absorbency of the different samples is shown in Figure 7. From the figure it was found that the modified SCBF has very low water absorption capacity within 36 h and remain same after 12 h. But for the synthesized copolymer and composite, the super absorbency is maximum and it increases with time till 36h. It is due to the hydrophilic nature of both PHEMA and PAM in the copolymer and maximum in the composite due to the porosity nature of the composite which is clearly seen in SEM Fig and hydrophilic nature of PHEMA, PAM and MMT.

**Fig 5** Water absorbency of (a) modified SCBF, (b) copolymer SCBF-g-Poly (HEMA-co-AM), and (c) composite SCBF-g-Poly (HEMA-co-AM)/MMT
Biodegradation
The biodegradation of modified SCBF, the copolymer SCBF-g-Poly (HEMA-co-PAM) and the composite SCBF-g-Poly (HEMA-co-PAM)/MMT in the soil burial test (Fig 6), sludge water (Fig 7) are shown. Weight loss due to the microbial degradation for SCBF in two cases is very small as compared to the synthesized eco-friendly composite which is more than that of the copolymer. This is due to the availability of good environment for growth of microbial which is supported by increase in water absorbency. It is due to the hydrophilic nature of PAM and PHEMA.

CONCLUSION
In the present study, SCBF-g-Poly (HEMA-co-AM) copolymer and its MMT composite SCBF-g-Poly (HEMA-co-AM)/MMT were synthesized successfully. Their characterization was done along with some properties like metal ions sorption, water absorption, and biodegradation. The formation of
the copolymer and the composite was confirmed by FTIR and SEM. On comparison of their properties, it is found that the composite showed the better metal ions sorption, water absorbency, and biodegradation. In comparing the results obtained in the sorption of heavy metal ions by composite, sorption is more in case of Fe$^{3+}$ ions which can be used as highly economic and efficient material for removing metal ions from waste water before disposing it to water reservoir. More and more research are required to enhance the adsorption properties of waste materials using acrylic monomers for better commercialization.

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REFERENCES


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