

Novel Biomaterials – Commercialization Approach

Biomaterials have been found to be associated with drawbacks related to less sorption efficiency and stability, restricting their commercial use (Pagnanelli et al. 2000; Scowronski et al. 2001). Sincere efforts toward structural modifications on the biomaterials leading to the enhancement of binding capacity and selectivity are, therefore, in great demand. A special emphasis is to be paid on green chemical modifications resulting in *tailored biomaterials* improving its sorption efficiency and environmental stability and thus making it liable for its commercial use as simple, fast, economical, eco-friendly green technologies. Attention has been paid by various research groups (Tsezos 1985; Saito et al. 1991; Gardea-Torresdey et al. 1998) to increase the sorption capacity of biomaterials for abatement of different metal ions. Klimmek and Stan (2001) reported that the maximum sorption capacities of the alga *Lyngbya taylorii* could be increased significantly after phosphorylation of the biomass. Bai and Abraham (2002) noted that the sorption ability of the fungus *Rhizopus nigricans* for Cr(VI) is also improved after the introduction of carboxyl and amino groups. The pretreatment of biomass with surfactants and cationic polyelectrolyte and deacetylation treatment of amino groups of chitin are favorable for abatement of metal ions (Tan and Cheng 2003). Pretreatment methods using different kinds of modifying agents such as base solution, organic acid solutions, and oxidizing agents have been used for the purpose of removing soluble organic compounds. Increase in efficiency of metal adsorption has been recently performed by many researches (Taty-Costodes et al. 2003; Gupta et al. 2003; Min et al. 2004; Acar and Eren 2006; Abia et al. 2006; Wankasi et al. 2006; Hannafiah et al. 2006). These chemical modifications in general improved the adsorption capacity of biomaterials probably due to higher number of active binding sites after modification, better ion exchange properties, and formation of new functional groups that favor metal uptake. The semi-synthetic biomaterials are deemed to be good candidates for their commercial use as biomaterials for removing toxic metals from wastewater with high adsorption efficiency.

Natural biomaterials are biodegradable and cannot be used for long-term applications for sorption as sorbent regeneration is necessary for cost-effectiveness. Therefore, constructive efforts toward enhancement of binding capacity and simultaneously increasing stability of sorbents for the improvement in their mechanical strength are the keen goals of the scientific community. Graft co-polymerization is

relatively a new technique in which one structure moiety is grafted on another structure moiety resulting in the formation of grafted co-polymer with above desired properties. Graft co-polymers are recognized for special properties including high strength, thermal stability, biodegradability, and non-toxicity (Ramakrishna et al. 2005). Many of the graft co-polymers of the present inventions are novel and are ideally suited for sorption. Polymer blends give rise to new polymeric properties. The invention relates to a process for grafting an alkyl acrylate to a polycarbonate, polysaccharides, and other cellulosic materials in the solid phase (Wada et al. 2006). The graft co-polymerization process can be adapted to be carried out in either a batch, semi-batch, or continuous mode. The polymers derived from the unique process of this invention are useful in paints, adhesives, stabilizers, composites, bulk polymers, bulk plastics, bulk elastomers, fabrics, fibers, and fillers for sterilizable packaging, metal coatings, and solidified sorbing surfaces (Zumei and Ramakrishna 2006). Baxo-Xiu et al. (2006) prepared a graft co-polymerization of acrylic acid and acrylamide which was capable of removing Cu(II) from aqueous solutions with high removal efficiency and a regeneration of seven successive cycles without any loss in metal uptake. In another study, Hashem (2006) grafted sunflower stalks with acrylonitrile using KMnO_4 as redox initiator. Similarly Shibi and Anirudhan (2002) grafted acrylamide onto banana stalk, which increases the adsorption capacity of the biomaterial from 138 to 210 mg^{-1} for Hg(II). Thus grafting improves the adsorption capacity, selectivity, and stability of the biomaterial by forming many reactive groups on the polymer (Bicak et al. 1999; Liu et al. 2002; Orlando et al. 2002; Guclu et al. 2003; O'Connell et al. 2006).

Recently, Goyal and Srivastava (2009) and Kardam et al. (2009) have modified sorption efficiency, simultaneously increasing regeneration cycle of various agricultural wastes using synthetic modification including graft co-polymerization.

Synthetic Modifications onto Biomaterial to Increase Its Sorption Efficiency for Cationic Metals

Strengthening of Bioactive Functional Group [COO⁻]

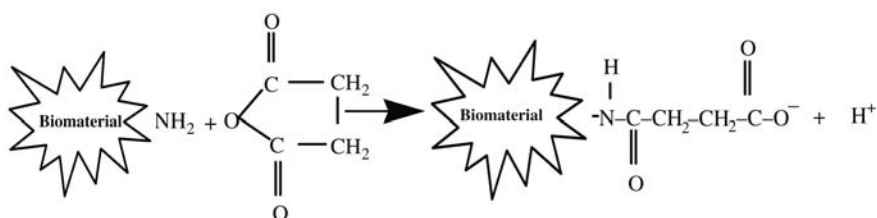
It is inferred that carboxyl ligands are important in the binding of metal ions. Thus increasing the number of such groups should increase the biomaterial binding ability. This is achieved through normal chemical reaction using mono-, di-, and tri-carboxylic acids or anhydrides.

Reaction with Anhydrides

The succination of the amino groups on the biomaterials is to be achieved by washing biomaterials first in HCl to remove any debris, followed by washing in sodium

acetate at pH 8.0. The biomaterials are to be suspended in $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ at pH 8.0. Succinic anhydride should be added to the suspended biomaterial. An additional succinic anhydride is to be added after 15-min intervals for the next 1½ h (six additions of succinic anhydride to the biomaterial). The biomaterial should be washed with HCl, centrifuged, and washed again with deionized water. Although the amino group is neutralized, it now forms an additional carboxyl group. By the addition of a carboxylate group, there should be an enhancement of metal binding by those metals that bind to carboxyl ligands. Succination of the biomaterial is performed to add a carboxyl group onto the nitrogen ligand. Sorption studies on this modified biomaterial show increase in sorption efficiency. This increased sorption may be ascribed to the addition of carboxylate ion.

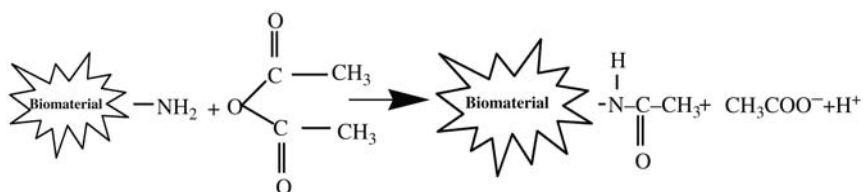
Succination of the biomaterial can be represented, in general, as follows:



Acetylation of amino group on the biomaterials is to be achieved by washing biomaterial first in HCl to remove any debris, followed by washing in sodium phosphate/sodium acetate buffer solution ($\text{Na}_3\text{PO}_4/\text{NaC}_2\text{H}_3\text{O}_2$) at pH 7.2. The biomaterials should be reacted with acetic anhydride and stirred while maintaining the pH of 7.2 for 1 h. The acetylated biomaterials will be next centrifuged for 5 min at 100.62 g. After removing the supernatant, the biomaterials are to be resuspended in hydroxylamine to remove *O*-acetyl groups. The biomaterials should be washed with HCl to remove any more soluble materials and finally washed with deionized water.

Acetylation of the biomaterial by acetic anhydride blocks the available amino ligands and decreases the number of positively charged sites on the biomaterial surface. This synthetic amendment reduces interference of the amino group, finally resulting in the increase of sorption of cationic metal species.

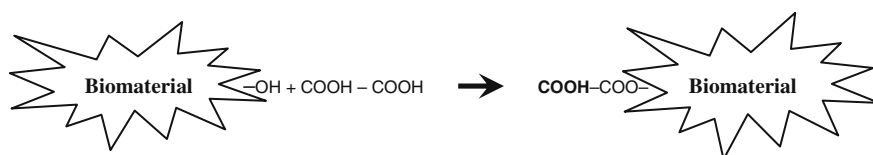
In general, the above fact can be represented as follows:



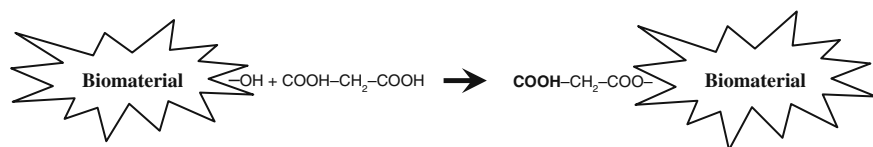
Reactions with Acids

The synthetic modifications of biomaterial (SMOS) powder were carried out with different acid solutions (oxalic acid, succinic acid, malonic acid, tartaric acid, and citric acid) in 1.0 M concentration in the ratio 1:5. Each modified biomaterial was used to monitor for the enhancement in their sorption efficiency for different cationic metal ions.

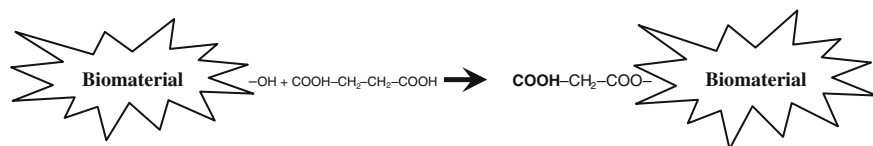
Oxalic Acid Modified SMOS



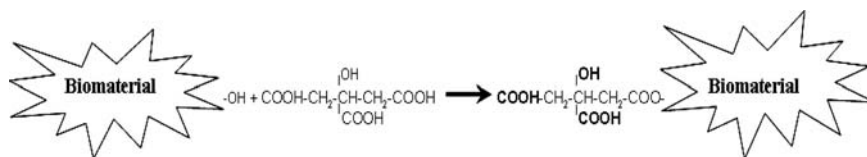
Malonic Acid Modified SMOS



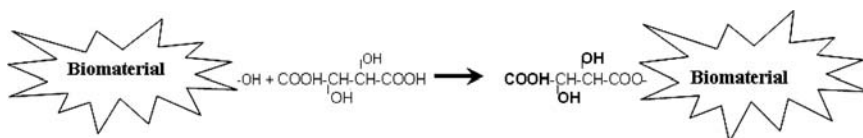
Succinic Acid Modified SMOS



Citric Acid Modified SMOS



Tartaric Acid Modified SMOS



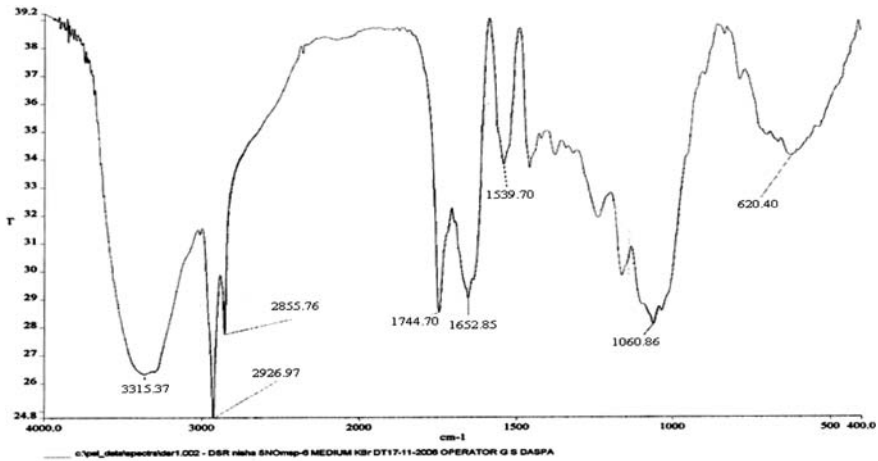
Evidence in Support of Chemical Modifications Occurring on Biomaterials Leading to Enhanced Sorption

FTIR analysis in solid phase in KBr is to be performed using a Fourier transform infrared spectrometer. Spectra of the sorbent before and after modifications should be recorded. Representative IR spectra of untreated and succinated biomaterial show the presence of additional peak of carboxylate ion [$1,744.70 \text{ cm}^{-1}$] and conversion of amino to amide group [$3,289.77\text{--}3,315.37 \text{ cm}^{-1}$] in succinated LLSP (*Leucaena leucocephala* seed powder), confirming succination of the LLSP biomaterial (Spectra 1). The conversion of amino to amide group [$3,289.77\text{--}3,365.14 \text{ cm}^{-1}$] confirmed the acetylation process (Spectra 2).

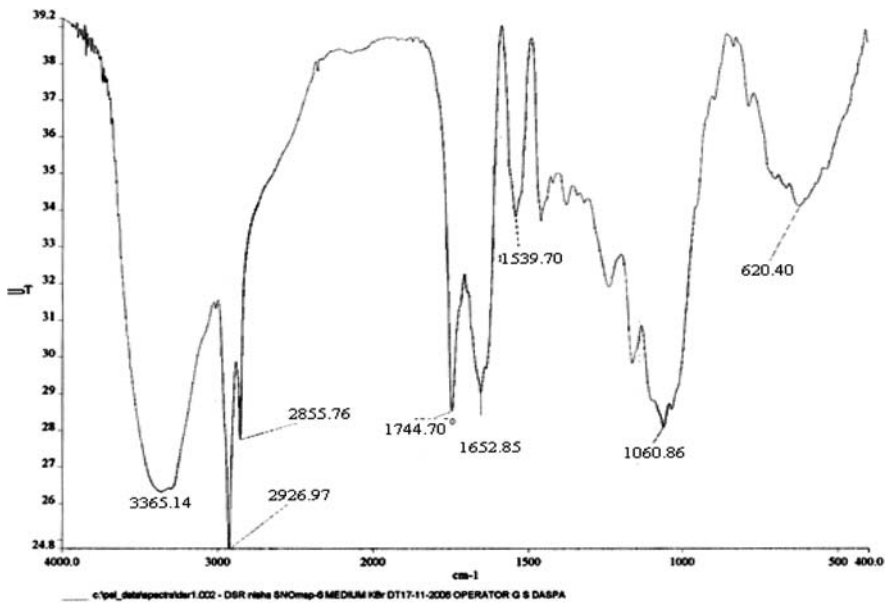
Increase in sorption efficiency and number of regeneration cycles of the chemically modified biomaterial is to be monitored.

Evaluation of Enhanced Sorption Efficiency of Modified Biomaterial

All the modified biomaterials are to be subjected to the assessment of sorption efficiency for cationic metals under previously standardized optimum conditions. The treatment of oxalic, malonic, succinic, tartaric, and citric acids with the biomaterial



Spectra 1 IR spectra of succinated *L. leucocephala* seed powder (LLSP)



Spectra 2 IR spectra of acetylated *L. leucocephala* seed powder (LLSP)

is an esterification process, introducing a carboxyl group to the product (Fig. 1). The introduction of such additional carboxyl ligands (COO^-) may be ascribed to the increased sorption potential for positively charged metal ions. The different chemically modified biomaterials showed the following order of increase in sorption potential for cationic metals in the range of 8–10%.



Fig. 1 Unmodified SMOS and different chemically modified SMOS

Oxalic < Malonic < Succinic < Tartaric < Citric Acid Modified Biomaterial

The order may be explained on the basis of increase in one carboxylic ligand with successive increase in the length of alkyl chain (oxalic acid to succinic acid) which is likely to increase the surface area of the biomaterial and result in successive higher sorption. Further increase in the sorption in citric and tartaric acid modified biomaterial may be described due to increase in the number of carboxylic ligands (tartaric acid –1, citric acid –2) along with other negatively charged bioactive OH groups. Such modification increases the total negative charge on the surface of the biomaterial resulting in further improved sorption.

Graft Co-polymerization

It was inferred that carboxyl ligands are important in the binding of metal ions, thus increase in the number of these groups should increase the biomaterial binding ability. This is achieved through graft co-polymerization of biomaterials using standard polymerization techniques and bulk of COOH groups were introduced at the surface.

For grafting, the biomaterial is to be dispersed in a definite amount of water. Appropriate initiators (ceric ammonium nitrate/ammonium persulfate/potassium persulfate) and nitric acid are to be added slowly to the reaction mixture. Appropriate monomers (acrylic/maleic/itaconic acid) should be added dropwise to the reaction mixture from the dropping funnel. The reaction flask is to be placed in a water bath at 100–85°C for various time periods under stirring by a magnetic stirrer. After a definite time period, the reaction mixture is to be filtered and the polymer should be removed with excess water. The grafted sample is to be dried to a constant weight and used for sorption studies (Figs. 2, 3, and 4). From the increase in weight of the biomaterial, percentage of grafting should be calculated as follows: % grafting = $(W_2 - W_1) / W_1 \times 100$, where W_1 and W_2 denote the weight of native and grafted biomaterial after complete removal of the homo-polymer, respectively.

Graft Co-polymerization with Acrylic Acid

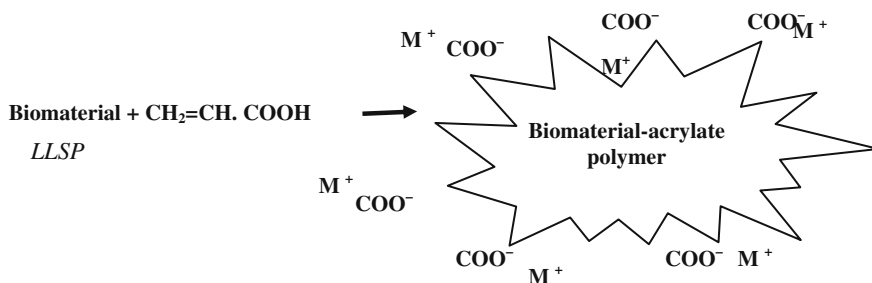
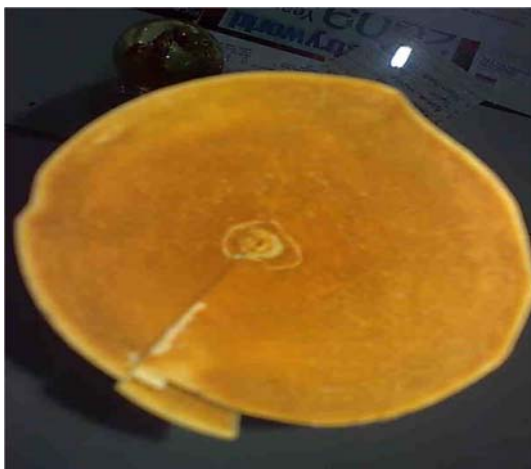


Fig. 2 Acrylic acid-grafted LLSP



Fig. 3 Maleic acid-grafted SMOS



Graft Co-polymerization with Maleic Acid

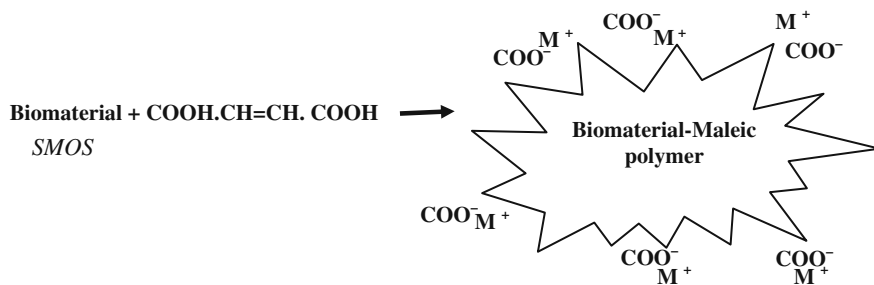
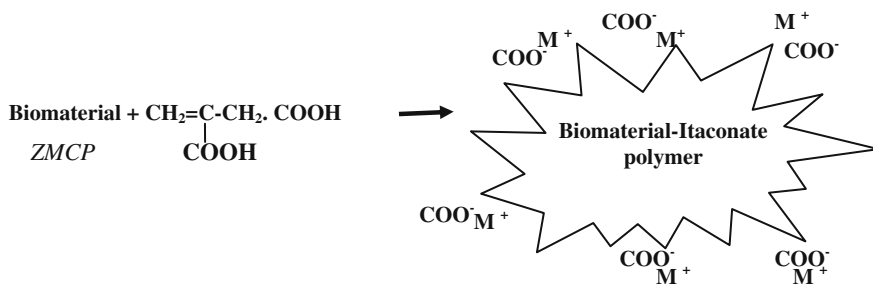


Fig. 4 Itaconic acid-grafted SMOS



Graft Co-polymerization with Itaconic Acid



Graft co-polymerized biomaterials exhibited maximum metal sorption potential. This is mainly due to the bulk of COOH group introduced at the surface. Grafting of the bulk of COOH groups onto the biomaterial becomes the basis of the increase in sorption efficiency in the range 15–20% for the abatement of different metal ions.

Evidence in Support of Improved Environmental Stability of the Biomaterial

The comparison of initial decomposition temperature (IDT) and final decomposition temperature (FDT) of unmodified and graft co-polymerized biomaterial should be estimated with *thermograms*. Thermogravimetric analysis of untreated (native) and

graft co-polymerized biomaterials shows significant differences in the initial decomposition temperature (IDT) and final decomposition temperature (FDT). Upon grafting, temperature of biomaterial (SILP) is found to be increased (IDT: 37.94 to 49.32°C; FDT: 600 to 609.23°C), indicating that grafting with acrylic acid improves the stability of SILP biomaterial (Figs. 5 and 6).

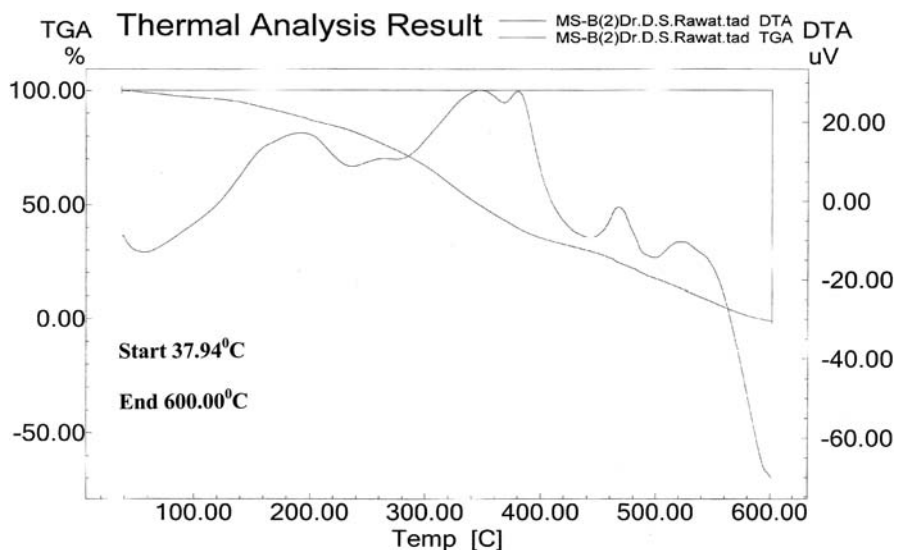


Fig. 5 TGA of ungrafted *Saraca indica* leaf powder (SILP)

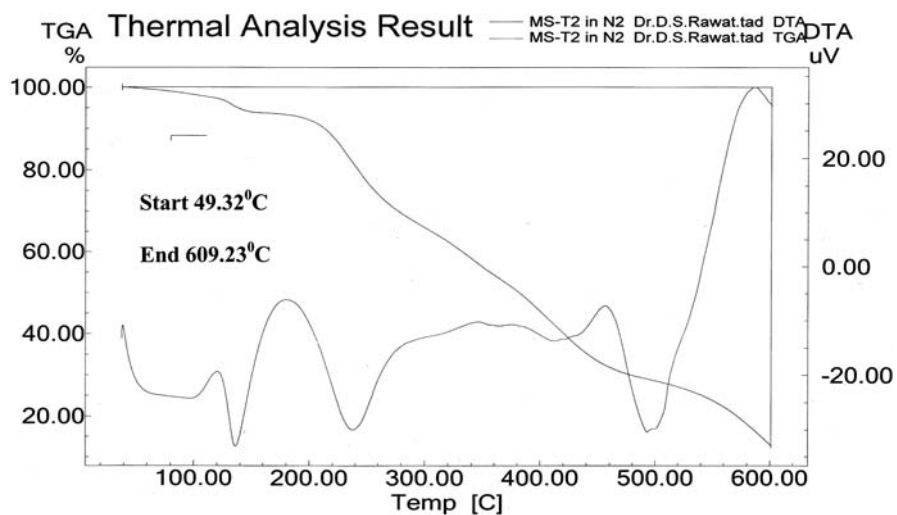


Fig. 6 TGA of acrylic acid-grafted *S. indica* leaf powder (SILP)

Table 1 Sorption of cationic metal ion on regenerated modified (graft co-polymerized) FRLP biomaterial

Cycles	% Sorption		
	Cd(II)	Cr(III)	Ni(II)
1	98.61	89.33	76.93
2	98.20	88.85	76.64
3	98.04	88.65	76.49
4	97.78	88.28	76.26
5	97.55	88.14	75.13
6	97.12	88.01	77.02

Increased stability of the graft co-polymerized biomaterials is to be monitored on the basis of increase in number of regeneration cycles. Table 1 clearly shows that structurally modified biomaterial (polymerized) can be used six times compared to only four times of the unmodified biomaterial (FRLP), exhibiting its increased environmental stability.

Synthetic Modifications onto Biomaterial to Increase Its Sorption Efficiency for Anionic Metals

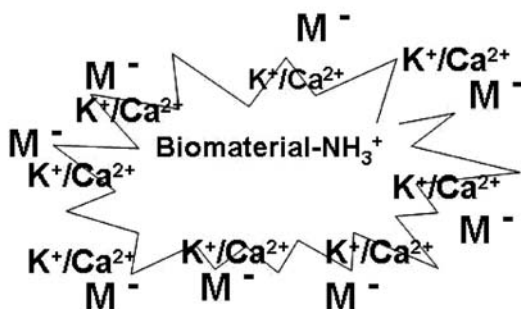
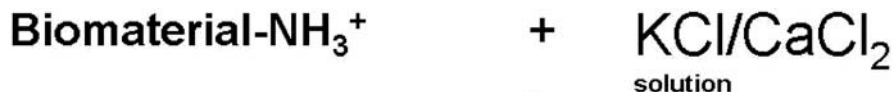
In order to use same biomass with enhanced sorption potential (ZMCP) for removing anionic metals also, different synthetic modifications have been carried out. The surface of the biomass has been made anion attracting by modifying with K^+ and Ca^{2+} ions. The surface of the cellulosic biomaterial (most of the time) in contact with water is negatively charged (Koshy et al. 2006). Ionic salts (KCl and $CaCl_2$) when dissolved in polar solvent like water then dissociate into ions (K^+ and Ca^{2+}) and these positive entities get deposited on the surface of biomass attracting negatively charged metal species.

Impregnation of Positively Charged Layer

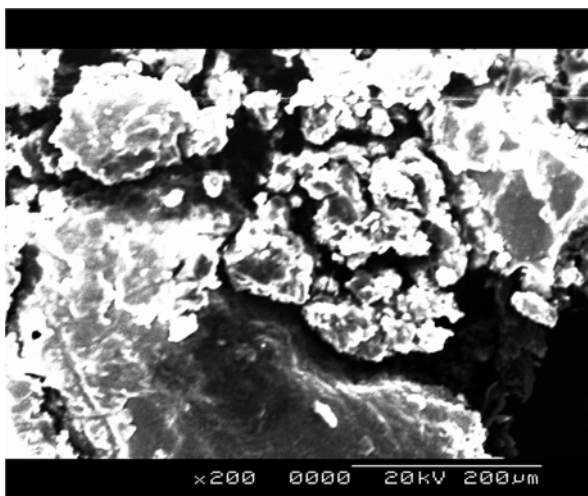
Experiments have been conducted with different biomaterials like *Zea mays* corn cob, *Moringa oleifera* seed powder and *L. leucocephala* seed powder as follows. A known amount of biomaterial powder was kept in contact with 200 mL solution containing 10.0 g of KCl/ $CaCl_2$ for 40 min. The solution was filtered and the solid material obtained was dried at $65^\circ C$ in the oven. The prepared powder was used for further experiment of sorption.

The formation of positively charged surface on the biomaterials was confirmed on the basis of SEM records (Micrographs 1 and 2).

Tables 2 and 3 provide data of enhanced sorption efficacy of impregnated biomaterials for Cr(VI) ions from water system.



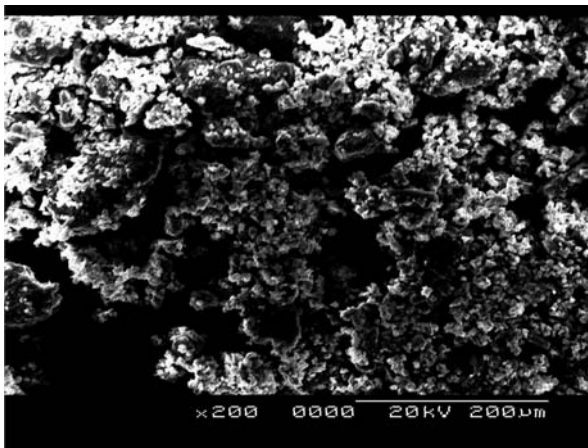
Enhancement in sorption of anionic metal



Micrograph 1 Scanning electron micrograph of native ZMCP showing large spherical cluster-type morphology

The data for Cr(VI) fitted well into both Freundlich and Langmuir isotherms. The magnitude of values K_f (0.12) and $1/n$ (0.28), Q_0 (3.91), and b (0.33) for ZMCP indicates the successful sorption of anionic metal species Cr(VI) (Figs. 7 and 8).

About 1,500,000 t maize is produced in India annually and the cobs are thrown as waste so the material is easily available practically at no cost. Therefore metal



Micrograph 2 Scanning electron micrograph of modified ZMCP showing dense agglomerated, etched cluster-type morphology

Table 2 Soluble Cr(VI) ion concentration (μM) after adsorption on *Z. mays* cob powder (ZMCP) as functions of contact time and biomass dosage at volume (200 mL), particle size (105 μm), and pH 2.5

Initial conc. mg/L (μM)	Soluble Cr(VI) concentration on powdered corncob			
	Biomass 0.5 g	Biomass 1.0 g	Biomass 2.0 g	Biomass 4.0 g
5 (19.23)	$14.76 \pm 0.69^{+\Phi}$	$12.38 \pm 0.50^{+\Phi}$	$10.92 \pm 0.52^{+\Phi}$	$10.96 \pm 0.56^{+\Phi\Phi}$
10 (38.46)	$25.26 \pm 1.13^{+\Phi}$	$21.11 \pm 1.01^{+\Phi}$	$18.57 \pm 0.77^{+\Phi}$	$18.65 \pm 0.95^{+\Phi\Phi}$
25 (96.15)	$48.34 \pm 2.07^{+\Phi}$	$41.15 \pm 2.01^{+\Phi}$	$36.26 \pm 1.84^{+\Phi}$	$36.34 \pm 2.25^{+\Phi\Phi}$
50 (192.30)	$96.46 \pm 5.11^{+\Phi\Phi}$	$82.07 \pm 4.59^{+\Phi\Phi}$	$72.11 \pm 3.89^{++\Phi}$	$72.26 \pm 3.54^{++\Phi\Phi}$
Correlation coefficient (<i>r</i>)	0.75	0.78	0.80	0.79

Numbers in parenthesis represent soluble metal concentrations in μM , standard deviations \pm , mean value difference (initial Cr(III) and Cr(VI) loaded versus soluble Cr(VI) (μM)) as functions of metal concentration; +significant ($p < 0.05$), ++insignificant ($p > 0.05$). Biomass dosage; Φ significant ($p < 0.05$), $\Phi\Phi$ insignificant ($p > 0.05$).

Table 3 Soluble Cr(VI) ion concentration in % sorption efficiency of impregnated shelled *Moringa oleifera* seed (SMOS) powder at volume (200 mL) and particle size (105 μm)

Biomaterial	Cr(VI) (%)
Native SMOS	88.15
Impregnated SMOS	91.09

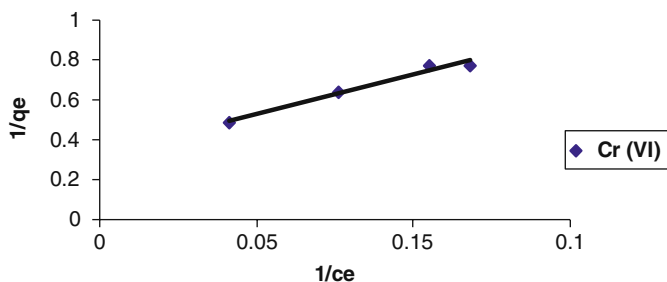


Fig. 7 Langmuir isotherm plot for the adsorption of Cr(VI) ion on impregnated ZMCP

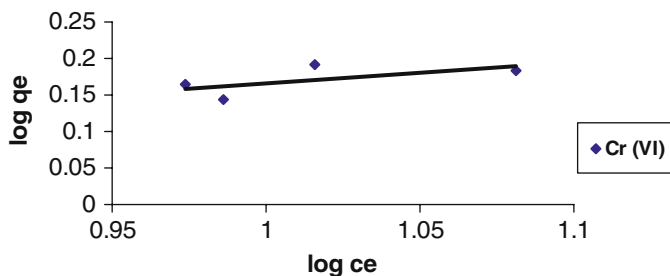


Fig. 8 Freundlich isotherm plot for the adsorption of Cr(VI) ion on impregnated ZMCP

sorption efficacy of modified *ZMCP* for different oxidation states of the metal ions provides a simple, efficient, instantaneous, and highly economical, eco-friendly method for removing toxic heavy metals from water bodies particularly for remote and rural areas.