



Characterization of novel *Zea mays* based biomaterial designed for toxic metals biosorption

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ABSTRACT

Structural modifications onto *Zea mays* Cob powder, ZMCP lead to the formation of novel biomaterial with increased sorption efficiency and environmental stability for the abatement of Pb (II), Cd (II), Ni (II) and Cr (III) in single as well as multi-metal ion solutions. Synthetic strategy for strengthening the functional groups, COO⁻ responsible for binding of metal species has been applied using acetylation, succination and graft co-polymerization processes. The resultant novel biomaterial exhibits enhancement in sorption efficiency from 2 to 15% and stability in terms of regeneration cycles from 3 to 5, evidence to support biomaterial designed has been provided on the basis of SEM, FTIR and TGA. The findings open up new avenues in the modern Green Technology of water treatment using biosorbent-possessing potential for commercialization.

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1. Introduction

Despite strict environmental rules and regulations for wastewater management, particularly in developing countries, industrial effluents released into water streams contain pollutants. Water pollution due to toxic heavy metals has been a major cause of concern for environmental engineers. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. The heavy metal pollution represents a significant environmental problem arising from its toxic effects and accumulation throughout the food chain. Cadmium, Chromium and Nickel are examples of heavy metals that have been classified as priority pollutants by the U.S. Environmental Protection Agency. In view of their high toxicity, environment mobility, non-biodegradability and stability, their removal becomes an absolute necessity. Among the possible reasons, the high cost and technical complexity of the treatment processes might be one of the important issues. Existing methods of wastewater treatment like ion exchange, electrochemical processes and membrane processes are associated with technical, economical, practical aspects and constraints like frequent change of filters, generation of large quantity of sludge that needs again safest disposal [1,2]. The search for new technologies for the removal of toxic metals has directed attention to biosorption phenomenon which is based on the metal binding capacity of agricultural wastes [3,4]. Recent researches indicate that the use of agricultural wastes has several drawbacks related to their lower sorption efficiency and stability for metal species, restrict-

ing their commercial use [5]. Agricultural wastes often, are also likely to transfer their respective color and odor to the water bodies. Constructive efforts towards enhancement of binding capacity and stability of sorbents are, therefore, in great demand. In general, functional structural moieties like carboxylic acid, amino acids, phenolic, hydroxyl groups etc. present in the biomaterials may constitute a physico-chemical active group of binding sites (working even at low concentration) to interact with metal ions and therefore, are supposed to be active sites for the sorption of metal ions. Strengthening of functional groups in the biomaterial may lead to the designing of novel biomaterial with enhanced sorption efficiency and stability.

The main objective of the present piece of work is the establishment of the basic structural moieties present in the *Zea mays* Cob powder, ZMCP biomaterial, responsible for sorption efficiency and then strengthening of functional group using various chemical modifications like acetylation, succination and graft co-polymerization leading to newly tailored biomaterials with enhanced sorption efficacy, environmental stability and increase in number of reusable cycle of the biomaterial for its reuse. The study suggests that development of such novel biomaterials can be suitable bioagents for the commercialization and removal of toxic metals from wastewater.

2. Experimental

2.1. Biosorbent preparation

Cobs of *Z. mays* were collected in June 2007. They were washed repeatedly with water to remove dust and soluble impurities, dried at 65 °C for 24 h, crushed and finally sieved through 105, 210 and

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420 μm mesh of copper sieves. No other chemical or physical treatments were used prior to the adsorption experiments.

2.2. Sorption studies

Sorption studies using standard practices were carried out in batch experiments in triplicates as functions of particle size: 105, 210 and 420 μm , biomass dosage: 2.0, 4.0 and 6.0 g, contact time: 10, 20, 30 and 40 min, metal concentration: 1, 5, 10, 25, 50 and 100 mg/l and pH 4.5, 5.5, 6.5, 7.5 and 8.5. The contaminated water was prepared using AR grade cadmium nitrate, nickel sulphate and chromium chloride in Erlenmeyer flasks. After pH adjustments, a known quantity of biosorbent was added and finally metal bearing suspensions were kept under magnetic stirring until the equilibrium conditions were reached. After shaking, suspension was allowed to settle down. The residual biomass sorbed with metal ions was filtered using Whatman 42 filter paper. Filtrate were collected and metal concentrations were determined using acetylene air flame Atomic Absorption Spectrometer (PerkinElmer-3100) using the equation: % Sorption = $(C_0 - C_e)/C_0 \times 100$, where C_0 and C_e are the initial and final concentration of metal ions in the solution.

2.3. Desorption experiment

Desorption studies were conducted to restore the biomass as a function of concentration of different desorption reagents: hard acid: 0.05 M HNO_3 and soft acid: 0.5 M citric acid. Metal loaded biosorbent obtained from our sorption experiments, were transferred to Erlenmeyer flasks and shaken with 50 ml of each desorption reagents as a function of time: 20, 40, 60, and 80 min at room temperature. At the end of each time interval the suspension was stirred for 5 min. The suspension was filtered using Whatman 42 filter paper and in the filtrate estimation of metal ion concentration was carried out.

The amount of metal ion remaining on the biomass as a function of time was calculated using a mass balance equation: $q_t = q_e - c_t$ (v/m), where, q_t and q_e are the biomass phase metal ion concentration (mg/l) and c_t solution phase metal ion concentration (mg/l) at time t (min) respectively.

2.4. Synthetic modifications onto ZMCP

2.4.1. Succination

The succination was achieved by washing 12.0 g of ZMCP first in 0.1 M HCl to remove any debris, followed by washing in 0.1 M sodium acetate at pH 8.0. The biomaterial was then resuspended in 500 ml of 1 M $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ at pH 8.0. 1.6 g of succinic anhydride was added to the suspended biomaterial. An additional 1.6 g of succinic anhydride was added after 15 min intervals for the next one and half hour (6 additions of 1.6 g of succinic anhydride to the biomaterial). The biomaterial was then washed with 0.1 M HCl centrifuged and washed again with de-ionized water.

2.4.2. Acetylation

Acetylation was achieved by washing 12.0 g of ZMCP first in 0.1 M HCl to remove any debris, followed by washing in 0.1 M sodium phosphate/sodium acetate buffer $\text{Na}_3\text{PO}_4/1.0\text{M}$ $\text{NaC}_2\text{H}_3\text{O}_2$ at pH 7.2. The biomaterial was reacted with 64.0 ml of acetic anhydride and stirred while maintaining pH 7.2. The acetylated biomaterial was next centrifuged for 5 min at 3000 rpm. After removing the supernatant, the biomaterial was then resuspended in 1 M hydroxylamine to remove O-acetyl groups. The biomaterial was then washed with 0.1 M HCl to remove any more soluble materials and finally washed with de-ionized water.

2.4.3. Graft co-polymerization

0.5 g of ZMCP was dispersed in 50 ml of water. 0.1 g of ceric ammonium nitrate and 1 ml of nitric acid were added slowly to the reaction mixture. Then 1.0 ml of acrylic acid was added drop wise to the reaction mixture from the dropping funnel. The reaction flask was placed in a water bath at 10–85 $^\circ\text{C}$ for various time periods under stirring by a magnetic stirrer. After 60 min, the reaction mixture was filtered and the homo-polymer was removed with excess water. The grafted sample was dried to a constant weight and used for sorption studies. From the increase in weight of the biomaterial, percentage of grafting was 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 ZMCP after complete removal of the homo-polymer.

2.5. Scanning electron microscopy (SEM)

The Scanning Electron Micrographs of unmodified and modified ZMCP were recorded at bar length equivalent to 200 μm at working voltage 20 KV with 200 \times magnifications.

2.6. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis in solid phase in KBr was performed using a Fourier Transform Infrared Spectrometer (FTIR-8400, Shimadzu). Spectra of the sorbent before and after modifications were recorded.

2.7. Thermo-gravimetric analysis (TGA)

The TGA was performed using Thermo Gravimetric Analyzer (DTG-60, Shimadzu). The comparison of Initial Decomposition Temperature, IDT and Final Decomposition Temperature, FDT of unmodified and graft co-polymerized biomaterial was estimated with thermo grams.

Sorption efficiency and number of regeneration cycles of the unmodified and chemically modified biomaterial was carried out in single metal: Pb (II), Cd (II), Ni (II) and Cr (III) as well as multi-metal solution using the procedure mentioned in our earlier publications [6–12].

2.8. Statistical analysis

Batch experiments were conducted in triplicate and data represents the mean value. Mean values, correlation coefficients, standard deviations were calculated using SPSS PC⁺ statistical package. For the determination of inter-group mean value differences, each parameter was subjected to the Student's t -test for significance level ($p < 0.05$).

3. Results and discussion

Sorption studies result into the standardization of the optimum conditions of biomass dosage: 2 g, particle size: 105 μm , metal concentration: 25 mg/l, contact time: 30 min and volume: 200 ml at pH 6.5. Maximum sorption for different metal ions was in single metal solution: Pb (II): 87.34%, Cd (II): 79.36%, Ni (II): 71.98% and Cr (III): 76.43% and multi-metal solution: Pb (II): 81.21%, Cd (II): 73.72%, Ni (II): 64.03% and Cr (III): 68.91%.

3.1. pH profile for metal ion binding

The effect of pH on the biosorption of metal ions on *Z. mays* Cob powder, ZMCP shows that the biosorption efficiency of the target ZMCP for metal ions in the pH range 2.5–4.5 did not vary significantly. However, there was a sharp increase in the sorption efficiency at further rise in pH from 4.5 to 6.5, thereby attaining a

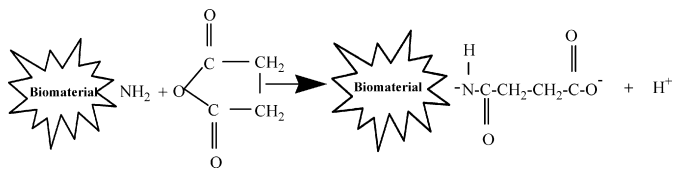


Fig. 1. Succination of *Zea mays* Cob powder.

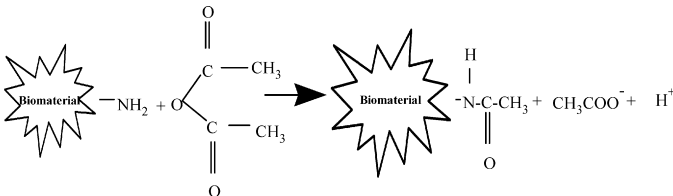


Fig. 2. Acetylation of *Zea mays* Cob powder.

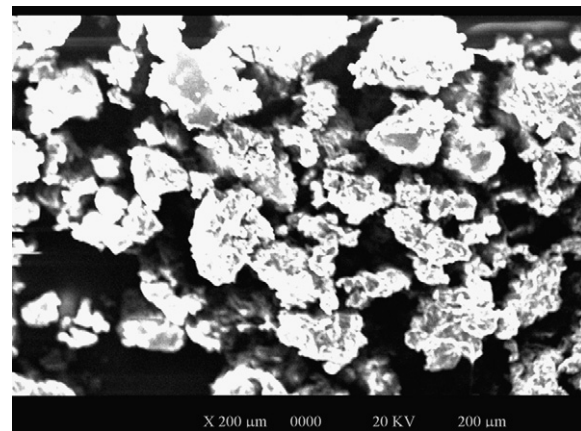


Fig. 5. SEM of acetylated ZMCP.

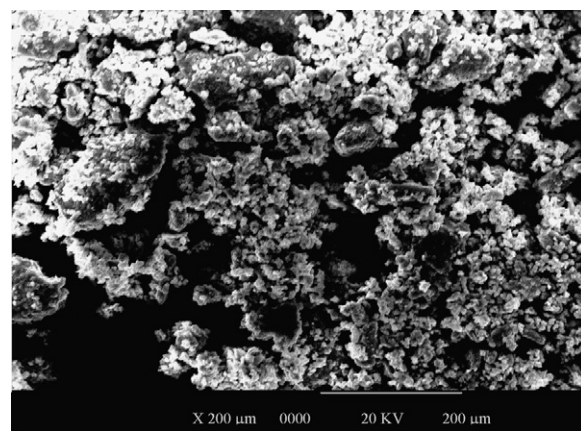


Fig. 6. SEM of succinated ZMCP.

maximum value at pH 6.5 and onwards. Investigation on pH variation beyond 7.5 yielded an apparent increase in sorption up to pH 8.5, which might be due to precipitation carry over of metal starting at pH 7.5 onwards [13].

The findings indicate that ZMCP has considerable potential to be used as biosorbent for metal removal from the aqueous system and require the understanding of the mechanistic aspects of interactions of seed biomass with metal ions. Based on our experimental findings, we synthesize a possible mechanism for metal binding to the biomaterial. The aqueous solution of ZMCP seed is a heterogeneous complex mixture possessing predominantly low molecular weight amino acids [14]. The proteinaceous amino acids have variety of structurally related pH dependent properties of generating appropriate atmosphere for attracting the metal ions [15]. Mechanistic aspect for metal biosorption is a rather complex process affected by several factors, among which pH of the solution is the most prominent. pH not only influences functional group dissociation but also influences the chemistry of metals in a solution. In

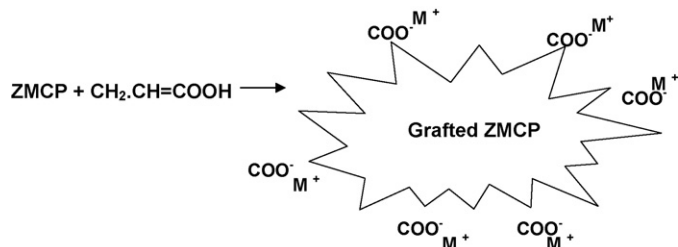


Fig. 3. Graft co-polymerization of *Zea mays* Cob powder.

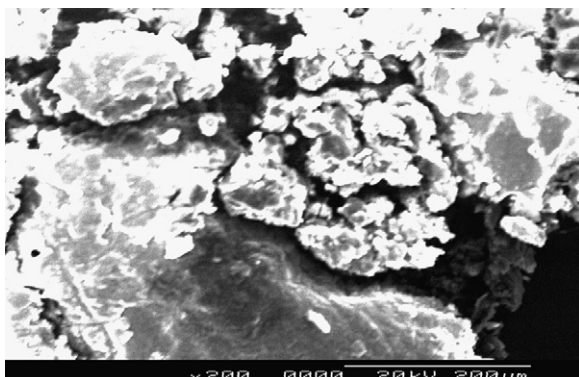


Fig. 4. SEM of untreated ZMCP.

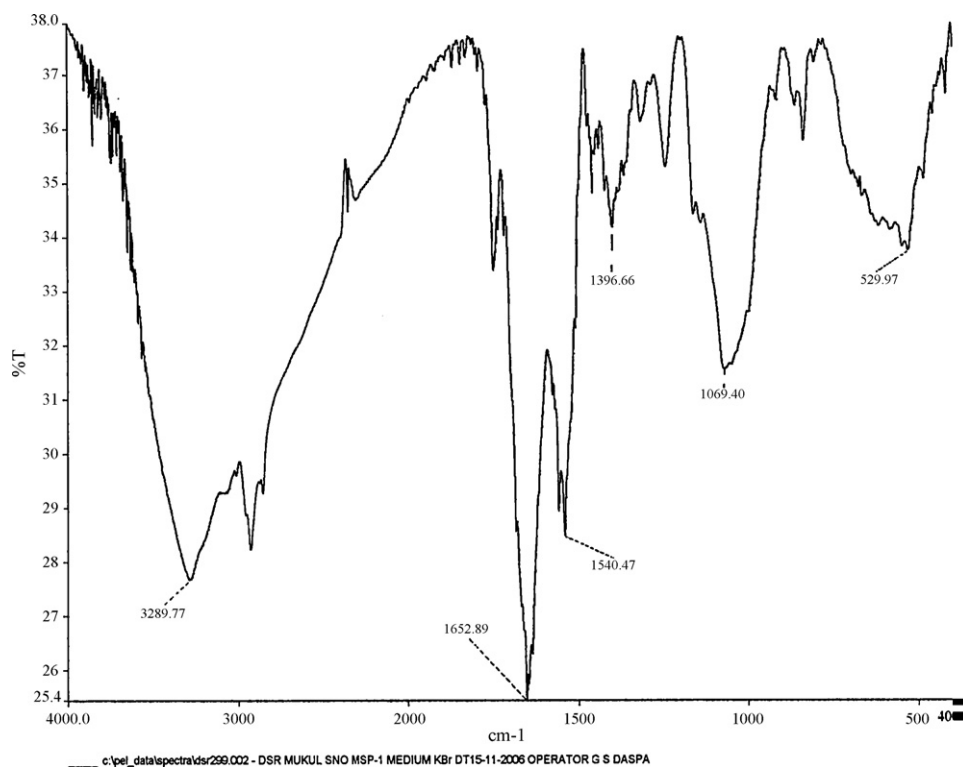
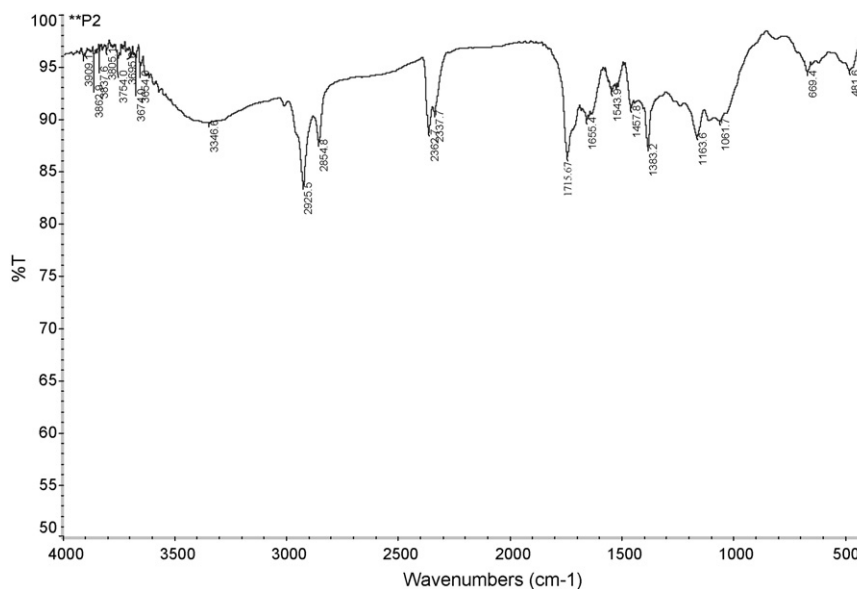
order to understand how metal binds to the biomaterial, it is essential to identify the functional groups responsible for metal binding. On the basis of our experimental findings and relevant literature, we synthesize a possible mechanism for metal binding to the ZMCP biomaterial. The majority of amino acids present in ZMCP have isoelectric point in the pH range 4.0–8.0. In this range of pH over 90% of the amino acid molecules are in the ionized state i.e. they have both positively charged amino groups and negatively charged carboxylic group. Carboxylate anion of the acid group has enough potential for binding cationic metal ions and become active sites for the sorption of M^+ ions.

It was found reasonable and logical to strengthen the functional group COO^- , responsible for sorption phenomenon by various chemical modifications to increase the efficiency of biomaterial to attract M^+ ion leading to its enhanced biosorption efficiency. Various strategies for this purpose are as follows.

Succination of the biomaterial is performed to add a carboxyl group onto the nitrogen ligand of the amino acid part of the biomaterial. Sorption studies on this modified biomaterial showed 5–15%

Table 1
Pore area (μm^2) of unmodified and modified ZMCP biomaterial.

Biomaterial	Pore area (μm^2)
Unmodified ZMCP	5.92
Succinated ZMCP	1.12
Acetylated ZMCP	1.56
Grafted ZMCP	1.89

Fig. 7. IR spectra of untreated *Zea mays* Cob powder.Fig. 8. IR spectra of acrylic acid grafted *Zea mays* Cob powder.**Table 2**

Enhancement in sorption efficiency of chemically modified ZMCP for cationic metals.

Metals	% Sorption			
	Unmodified	Succinated ZMCP	Acetylated ZMCP	Graft co-polymerized ZMCP
Single metal solution				
Pb (II)	87.34 ± 0.09	92.83 ± 0.05	89.04 ± 0.08	96.23 ± 0.05
Cd (II)	79.36 ± 0.06	86.67 ± 0.01	83.65 ± 0.06	92.48 ± 0.04
Ni (II)	71.98 ± 0.03	80.27 ± 0.02	78.32 ± 0.07	85.12 ± 0.06
Cr (III)	76.43 ± 0.02	84.71 ± 0.03	82.73 ± 0.03	89.42 ± 0.07
Multi-metal solution				
Pb (II)	81.21 ± 0.07	86.21 ± 0.08	83.71 ± 0.05	91.65 ± 0.06
Cd (II)	73.72 ± 0.04	79.82 ± 0.05	76.21 ± 0.07	84.03 ± 0.08
Ni (II)	64.03 ± 0.06	71.57 ± 0.07	68.23 ± 0.09	77.27 ± 0.05
Cr (III)	68.91 ± 0.03	76.71 ± 0.06	71.52 ± 0.07	83.46 ± 0.06

increase in sorption efficiency for metal ions studied. The enhancement of the sorption may be ascribed to the addition of carboxylate ion [Fig. 1].

Acetylated biomaterial also showed 2–8% increase in the sorption of various metal ions. Acetylation 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 into the increase of sorption of cationic metal species [Fig. 2].

Another synthetic strategy, graft co-polymerization was also applied to increase the number of negatively charged carboxylate groups onto the ZMCP biomaterial to enhance the ability to attract M^+ ions. It was achieved by grafting of negatively charged functional groups using standard polymerization techniques. The fact is explained as diagrammatically presented in Fig. 3. The polymerization of monomer acrylic acid resulted into grafted co-polymerized biomaterial.

3.2. Evidence in support of structural modifications onto biomaterial

3.2.1. Scanning electron microscopy [SEM]

SEM of the native and modified ZMCP was recorded and compared for the difference in morphology and reduction in pore area. SEM of the native biosorbent exhibits large spherical clusters while that of modified biosorbent represents dense, agglomerated, irregular type morphology. The change in morphology indicates the accumulation of liquid phase concentration of charge moieties onto ZMCP surface area [Figs. 4–6]. The fact is further supported by the reduction in pore area in the SEM of modified biomaterial [Table 1].

3.2.2. Fourier transform infrared spectroscopy [FTIR]

The comparison of the IR spectra of untreated and succinated biomaterial showed the presence of additional peak of carboxylate ion at 1744.70 cm^{-1} and conversion of amino to amide group from 3289.77 to 3315.37 cm^{-1} in succinated ZMCP confirming succination of the biomaterial.

The conversion of amino to amide group from 3289.77 to 3365.14 cm^{-1} confirmed acetylation process.

The appearance of characteristic peak at 1715.67 cm^{-1} ($C=O$) in the IR spectra of graft co-polymerized compared to its unmodified ZMCP confirms the formation of the grafted biomaterial [Figs. 7 and 8].

3.3. Sorption efficiency of modified biomaterial

All the three modified biomaterials were subjected to assessment of sorption efficiency for cationic metals in single and multi-metal solution under previously standardized optimum conditions. Increased sorption efficiency in all the three modified biomaterials has been observed with the same amount of biomaterial dosage: 2 g [Table 2].

TGA of unmodified and graft co-polymerized ZMCP biomaterial showed significant differences in the Initial Decomposition Temperature from 37.91 to $47.62\text{ }^\circ\text{C}$ and the Final Decomposition Temperature from 600.75 to $607.13\text{ }^\circ\text{C}$ [Figs. 9 and 10].

The difference in decomposition temperature of unmodified and polymerized biomaterial shows the polymerization on the biomaterial simultaneously indicating the enhancement of its stability. The increase in stability of the polymerized biomaterial was also reflected by the increase in number of cycles of its reusability. Polymerized biomaterial can be used 5 times compared to 3 times of native ZMCP biomaterial [Fig. 11]. It is inferred that out of 3 structural modifications considered for the study, graft co-polymerization not only maximized the sorption efficiency but also

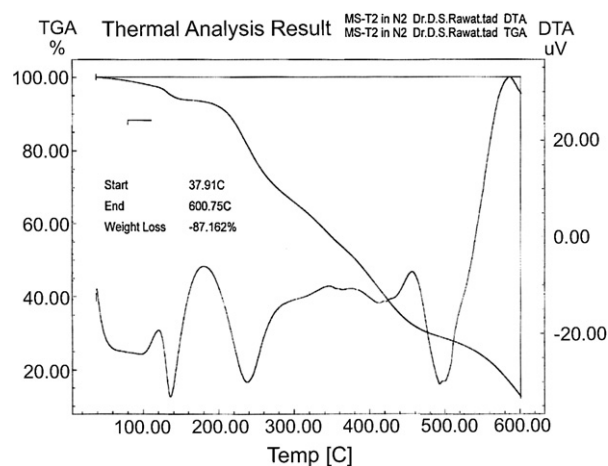


Fig. 9. TGA of ungrafted *Zea mays* Cob powder.

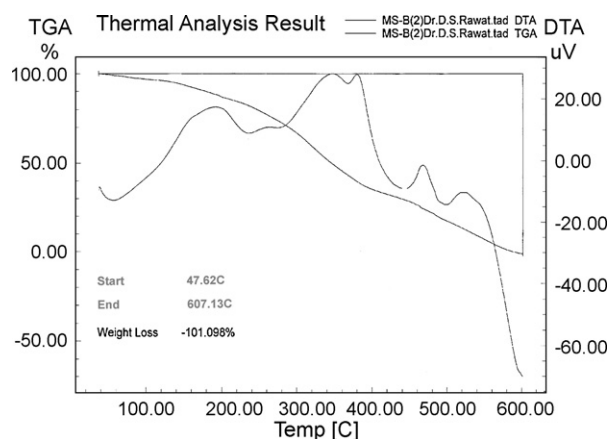


Fig. 10. TGA of acrylic acid grafted *Zea mays* Cob powder.

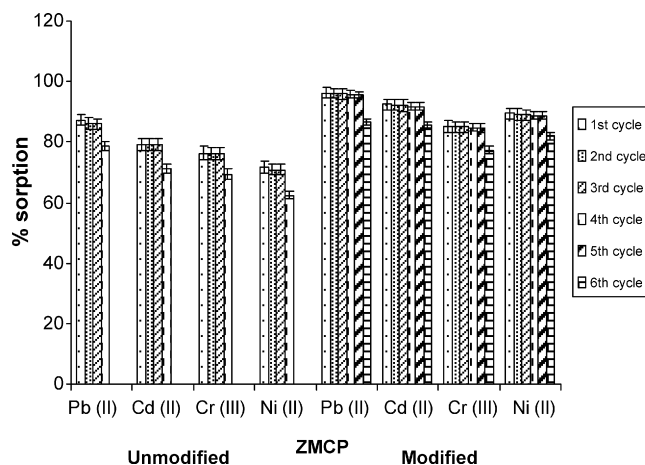


Fig. 11. Enhancement of reusability of the novel ZMCP biomaterial for different metal ions.

increased in number of cycles of its reusability, highlighting its cost effectiveness.

4. Conclusion

Commercial constraints for the commercialization of agricultural wastes as biosorbent were linked to their less biosorption efficiency, stability and number of its reusability. The proposed

physico-chemical scheme involves the strengthening of responsible biofunctional group using several chemical processes. This led to the development of tailored novel biomaterials having enhanced sorption efficiency and number of reusability. The biomaterials can be viewed as green, ecofriendly, fast and simple techniques under the domain of Green Chemistry for the decontamination of toxic metals from wastewater. *Z. mays* Cob powder is non-toxic, biodegradable, environmentally acceptable and available at practically little or no cost. When modified for its enhanced sorption efficiency, it provided exceptionally useful bioagent showing increase in its reusable cycles. Therefore, *Z. mays* Cob powder appears to be a good agricultural waste for the strengthening of bioactive functional group for sorption leading to the development of novel biomaterials for decontamination processes. It is a low cost pretreatment step before large chemical treatment for metal decontamination and presents alternative opportunity for high-tech methods and synthetic coagulants under the domain of Green Chemistry.

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