



Radiation Synthesis of Biopolymers for Removal of Zirconium (IV) from Aqueous Solution

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Abstract: This work explored the potential a cost-effective, simplistic and feasible method for commercial purposes to make sawdust polymeric films for zirconium Zr (IV) ions removal from aqueous medium. In this regard, cellulose acetate (CA) -co- Poly glycidyl methacrylate (PGMA) was prepared via radiation induced graft polymerization. The effect of sawdust content (SD) (wt%) on the properties of CA-co-PGMA biopolymer films was studied. The structural investigations and applicability of the prepared CA-co-PGMA/SD biopolymer films were carried out using XRD, SEM, FTIR, EDX and ICP. The introduction of more ionizable groups into the prepared biopolymer by NaOH-treatment regulated in improving its properties compared to untreated ones and these properties depend mainly on the number and form of the ionizable groups. Removal of zirconium (IV) from its aqueous medium was studied in batch mode experiments. The results of this study indicate that modification of CA-co-PGMA/SD biopolymer films shows great potential for simultaneous removal adsorptive of zirconium ions from its aqueous solution. Also, the prepared biopolymer has high efficiency for separation of Ti (IV) ions from its aqueous mixture with Zr (IV) ions.

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1. Introduction

Recently, many articles have studied the capability of using low-cost biopolymer for treatment of contaminated wastewater containing toxic heavy metals ions [1-3]. The usage of biopolymer in wide industrial range is still limited as the lack of their mechanical properties and their chelating affinity toward metal ion [4,5]. Physical and chemical treatment methods such as mixing, cross linking and grafting, with activated compounds are have been used to modification of biopolymer properties [6,7]. Chitosan zirconium tungstate bionanocomposite was fabricated to be used as catalytic agent for degradation of anionic and cationic dyes in addition to their binary combinations [8, 9].

Many biosorption methods use biomaterials as marine algae [10], industrial wastes and in biological procedures like fermentation [11, 12], initiated mud [13, 14] and stimulated charcoal [15]. The application of biosorption process in the waste water treatment is considered as one of the encouraging replacements, in this regard, the main factors for the choosing a biosorbent are including rapid rate of metal uptake, high affinity, and extreme loading ability [2]. So, there is a great attention are given for identification of novel and superior biosorbents which possessing the ability for adsorbing metal ions [16, 17].

The addition of sawdust with various polymer had been literature, low-cost Sawdust-Polystyrene (SD-PS) composite [18, 19] and developed to prepare superhydrophobic pellet for efficient oil-water separation [20]. Many authors studied mechanical properties of ceramic bricks and the impact of sawdust on the petrophysical characteristics of solid bricks [21, 22].

Cellulose acetate (CA) is a thermoplastic material which produced from highly purity cellulose and has various applications [23]. Cellulose acetate has low chemical and thermal resistance and mechanical properties. To improve the properties of cellulose acetate membranes, polyethelene glycol (PEG 600) had been added [24, 25].

Zirconium is mostly used as a refractory and pacifier [26-28], because of its strong corrosion resistive Zirconium, is used in small amounts as an alloying agent [29, 30]. It also is a key manufacturing substance to perform a definite industrial process and is mostly applied in the making of light filaments [31], surgical appliances [32, 33], photoflash bulbs [34, 35], molds for molten metal's [36] and tanning of leather [37-39]. Zirconium is characterized by its relatively high transparency to neutrons and therefore it is

considered an important manufacturing substance in the field of nuclear energy [40-43].

In present study, cellulose acetate-co-polyglycidyl methacrylate/ sawdust biopolymer films were prepared by gamma radiation induced polymerization. The prepared film were tested to be applicable as adsorptive material for Zr (IV) from aqueous solution.

1. Experimental Materials

Cellulose acetate (CA) and Glycidyl methacrylate (GMA) of purity 99% (Aldrich). Sodium Hydroxide, (purchased from Sigma Aldrich). Wood sawdust (SD) (obtained from wood-working practices in Egypt), Other chemicals were reagent grade, not required more purification.

Preparation of Cellulose acetate-polyglycidyl methacrylate/ sawdust (CA-co-PGMA/SD) biopolymer films

The total copolymer concentration used is 6g of composition 70/30wt% (CA/ GMA) in 100ml dimethyl formamide (DMF). Firstly, CA was dissolved in DMF then GMA was added. Various contents of sawdust (2,5, 7, 10 and 12 wt%) was introduced, 30wt% of PEG was added as a plasticizer. In the preparation of CA-co-PGMA/SD biopolymer film, the film becomes brittle as the sawdust content exceed 12wt% and cracks easily. So, we couldn't able to increase the amount of sawdust upon 12wt%. The prepared solutions were exposed to different radiation doses. After irradiation, a volume of 30 ml of each combination were casted uniformly onto the surface of glass petri dishes (12 cm in diameter), and left to dry at 50°C for 24 h in hot air oven. Finally, the formed films were dragged from the surface of Petridishes and preserved in polyethylene bags to prevent pollution.

Alkaline Treatment of the Prepared Films

Enhancement of the characteristic of the prepared biopolymer films particularly, hydrophilic an ion exchange belongings was performed via treatment of the biopolymer with NaOH (5wt %) aqueous solution at 50°C for 2h using a reflux system. Then, the treated films were washed in distilled water and in dist. Water for 24h to eradicate the leftover of reagents, and finally dried at 50°C for 24h in hot air oven.

Gamma Radiation Source

The samples of biopolymers were irradiated with a dose of 0.4kGy/h. of ⁶⁰Co gamma rays (γ -cell) produced by the atomic energy of India and constructed by National Center for Radiation Research and Technology, Cairo, Egypt.

Characterization of the nanocomposite films Scanning electron microscope (SEM) Surface morphology of the specimens was investigated using JEOL JEM- 5400 (Japan) scanning electron microscope after gold deposition in vacuum for 3 min.

Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis of the prepared biopolymer

films was determined in the wave number range 4000 and 400 cm^{-1} , at a resolution of 4 cm^{-1} , using a Bruker Vertex 70 FTIR spectrophotometer.

X-Ray diffraction (XRD)

Shimadzu Diffractometer (XRD- 6000) of 30 mA and 40 kV at Cu $K\alpha$ ($\lambda=1.54 \text{ \AA}$) was used for measurement of XRD. Measurements were carried at scan speed 8°/min. and diffraction angle (2θ) range of 4–90° at room temperature.

Mechanical properties

Specimens of 50mm length and 4mm neck width, in the form of dumbbell-shaped were taken for estimation of elongation at break and ultimate tensile strength. The measurements were carried out by using Hounsfield (model H10 KS) tensile testing apparatus and performed at room temperature. The biopolymer films were determined at 10 mm/min speed and analyses were performed with a 20 kN load cell.

The Inductively Coupled Plasma-Mass (ICP-MS)

The analytical measurement of Zr (IV) concentration in aqueous solution was carried out by ICP-MS a NexION 300 D (Perkin from the Haier Basin, Elmer, USA). The analysis was done in triplicate.

Energy Dispersive X-ray analyzer (EDX)

In the current study, A JEOL 5400 scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) attachment (Japan) were used. The prepared biopolymer film was immersed for 3h in the solution mixture of two metal ions (Zr (IV) and Ti (IV)) with initial concentration 20ppm for each metal ion. Then the membranes were cleaned with distilled water and left for drying in a vacuum hot air oven at 50°. The competitive adsorption of the biopolymer films was tested.

Statistical analysis

All the obtained data were statistically analyzed using the ONE-WAY ANOVA at $P < 0.05$. Differences between means were analyzed by Duncan's multiple range tests using IBM-SPSS software version 24 as a statistical resource.

Result and discussion FTIR

Figure (1) shows the FTIR spectra of SD, CA-co-PGMA and CA-co- PGMA/SD/Zr (IV) biopolymer films that treated with NaOH. The chief components in SD is cellulose, the original SD displayed the characteristic beaks of cellulose backbone. The broad band around 3357 cm^{-1} is attributed to -OH stretching of hydroxyl groups, which creates from lignin, cellulose and hemicelluloses moieties of sawdust particles [44]. The intense peak at 1692 cm^{-1} and 1364 cm^{-1} were due to symmetric and asymmetric stretching peaks of carboxylate groups. The stretching prominent peak at 1096 cm^{-1} was attributed to C-O stretching. Similar peaks with different intensity and peak position were detected after incorporation of Zr (IV),

which was attributed to the interaction between Zr (IV) and CA-co-PGMA/SD polymer matrix (Fig.1c).

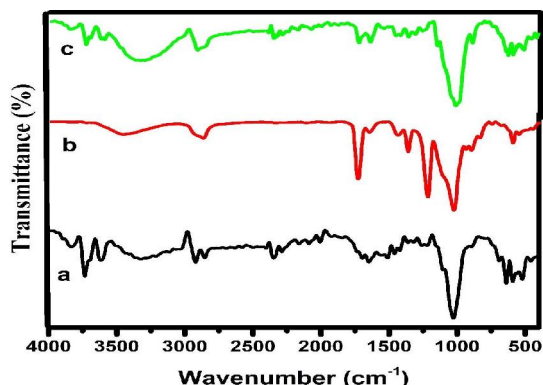


Fig. (1): FTIR of (a) SD, (b) CA-co-PGMA and (c) (CA-co-PGMA/SD that immersed in Zr (IV) ion;

treated with NaOH SD content; 7wt%.

SEM

SEM micrographs of CA-co-PGMA treated with NaOH, CA-co-PGMA/SD treated with NaOH and CA-co-PGMA/SD treated with NaOH that immersed in Zr (IV) ions were presented in Fig (2). The topography of CA-co-PGMA treated with NaOH film is smooth and has dense surface (Fig.2a) as demonstrated in the figure, but when sawdust is added great changes in the surface morphology were observed and the film exhibited to have a rougher structure. The surface morphology of biopolymer film containing 7wt% of SD showed like porous structure (Fig.2b) such pores almost disappeared after introduction of Zr (IV) (Fig.2c).

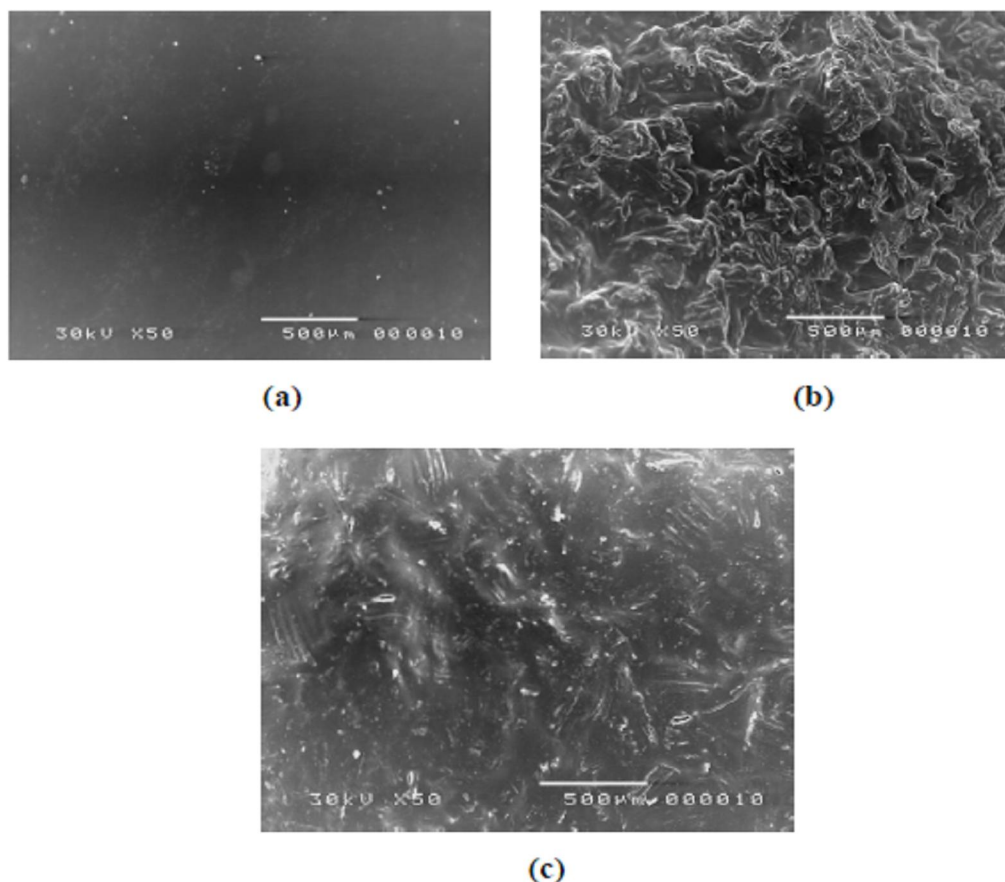


Fig. (2): SEM* of: (a) (CA-co-PGMA); (b) CA-co-PGMA/SD and (c) CA-co-PGMA/SD/ Zr (IV) treated with NaOH. *magnification X50

X-ray diffraction

The XRD patterns of sawdust (SD), CA-co-PGMA treated with NaOH, CA-co-PGMA/SD (7wt%) treated with NaOH and CA-co-PGMA/SD (7wt%) treated with NaOH/ Zr (VI) were presented in Fig.3. XRD patterns of SD appeared to have a semi-

crystalline structure and two intense peaks were observed at diffraction angle (2θ) = 16.44° and 22.6° which are parallel to (101) and (002) lattice planes of cellulose I [45, 46]. An additional tiny peak was verified at $2\theta=34.64^\circ$, attributing to (400) of crystalline cellulose I.

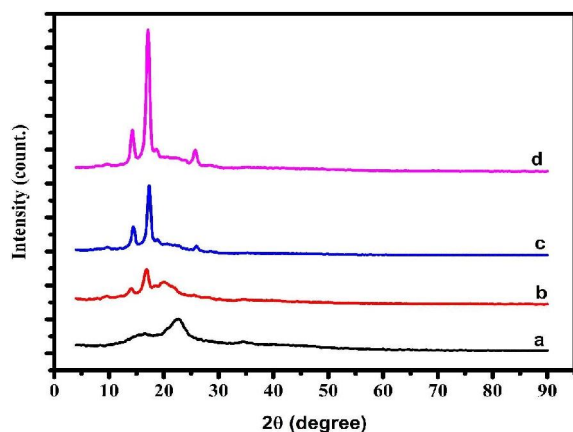


Fig. (3): XRD pattern for: (a) SD; (b) CA-co-PGMA treated with NaOH; (c) CA-co-PGMA/SD treated with NaOH & (d) CA-co-PGMA/SD/Zr (IV) treated with NaOH; SD content; 7wt%.

In the XRD pattern of CA-co-PGMA (Fig.3b) the same diffraction peaks as for SD were recorded related to cellulose and additional peak was appeared at 2θ of 17° which related to GMA.

The XRD patterns of CA-co-PGMA/SD (Fig.3c) and CA-co-PGMA/SD/Zr (Fig.3d) were similar with some differences observed at 2θ angle and their intensity; indicating that the intermolecular forces existing between molecules have an effect on deformation and crystallinity of the polymer chains. The remarkable increase in the peak intensity of CA-co-PGMA/SD/Zr reflects the increase in the crystallinity of the polymeric film. Thus the existence of Zr (IV) in biopolymer matrix enhanced the crystallinity of the resulting biopolymer film.

3.5. Effect of Irradiation Dose on Mechanical Properties

The data revealed that an increasing in the dose of irradiation was associated with an enhancement of tensile strength of the CA-co-PGMA/SD up to 30kGy beyond which the tensile strength decreases, however, the elongation (%) increase with irradiation dose (Figure 4).

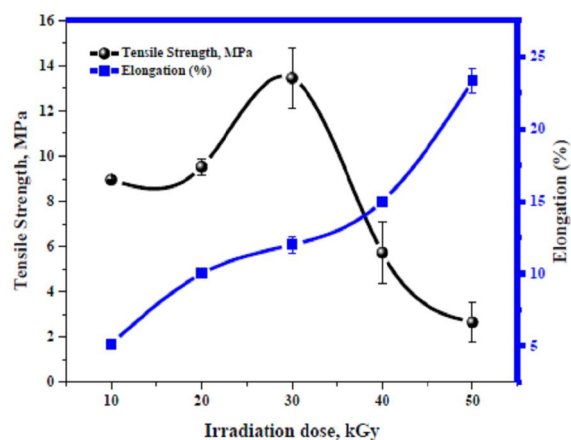


Fig.4: Effect of irradiation doses on tensile Strength (MPa) and elongation (%) of CA-co-PGMA/SD, SD content; 7wt%

The increase of tensile strength of the film due to the increase in cross linking density, as well as the formation of the chemical and physical interactions between the constituents of the biopolymer film. The marked decrease in tensile strength and increase in elongation percent at irradiation doses greater than 30kGy is attributed to chain scission of constituents of the biopolymer at such high doses. So, it can be concluded that CA-co-PGMA/SD copolymer prepared at a total irradiation dose 30kGy possessed acceptable mechanical properties for handling in practical uses.

Adsorption of Zr (IV) and Ti (IV) Ions:

Inductively Coupled Plasma-Mass (ICP-MS) and energy dispersive X-ray (EDX) are useful in giving quantitative and semi-quantitative estimation of absolute metal ions contents, respectively.

The adsorption of Zr (IV) ions individually and in a mixture with Ti (VI) ions using the prepared biopolymer containing different sawdust contents (wt%) was studied and the data are shown in Tables 1 & 2.

Table1. Effect of sawdust content (wt%) and alkali treatment of the prepared biopolymer on the removal (%) of Zr (IV) ion from aqueous solution; Zr (IV) conc.:20ppm at pH;6.4.

Sawdust content (wt %)	Removal (%)	
	CA-co-PGMA/Sawdust untreated	CA-co-PGMA/Sawdust; NaOH- treated
0	33.27±1.3	37.92±2.1
5	51.49±5.4	63.98±3.7
7	78.26±2.7	83.67±1.8
10	85.78±3.1	91.19±1.94
12	93.61±2.6	98.84±0.99

It was found that, adsorption process strongly dependent on the number and form of the ionizable

groups, size of the hydrated metal ions and the electrostatic interaction between the metal ions and

functional groups. Thereby, for mixtures of two metal ions, it is a competition process between the different metals and functional groups.

It is observed that the adsorption Zr (IV) or Ti (VI) ions increases with increasing sawdust content due to its relatively high surface area and abundant functional groups which enhances the adsorption process. For noncompetitive adsorption of Zr (IV), the removal percent reaches 98.8% which attained by NaOH-treated CA-co-PGMA/SD biopolymer film containing 12wt% of sawdust. Whereas, in the

competitive adsorption of Zr (IV) and Ti (IV) ions in a mixture, the removal percent for Ti (IV) was 98.08% and Zr (IV) was 1.92%. For the same biopolymer film, the results indicated that the prepared biopolymer film has high affinity toward Zr (IV) when it is present individually, contrary, it has high selective adsorption toward Ti (IV) when it was in a mixture of Zr (IV) + Ti (IV). From the obtained results the prepared CA-co-PGMA/SD biopolymer film containing 12wt% of sawdust can be use in separation of Ti (IV) from Zr (IV).

Table 2. Competitive adsorption (%) of Zr (IV) and Ti (IV) metal ions in a solution mixture contains 30ppm of each two metals

Sawdust content (wt%)	Removal (%)	
	Zr (IV)	Ti (IV)
7	19.8±2.47	80.2±1.36
10	7.9±1.32	92.1±2.98
12	1.92±0.91	98.08±3.05

Conclusion

It is demonstrated in this study a facile synthesis of CA-co-PGMA/SD biopolymer film using simultaneous radiation method followed by alkaline treatment. Its application in removal of Zr (IV) from its pollutant and separation of Zr (IV) /Ti (IV) mixture were investigated to find that CA-co- PGAMA/SD biopolymer film has high affinity toward Zr (IV) when it is present individually and the removal (%) reaches 98.8%. The adsorption capacity dependent on the content of SD particles in the biopolymer film. The results also indicated that the prepared biopolymer film has a abundant prospective to meet the requirements of various fields particularly separation of Zr (IV) /Ti (IV) from their mixture. SEM measurement showed that SD distributed homogeneously on the biopolymer film surface forming like porous structure. XRD diffractograms indicates that Zr (IV) improved packing of macromolecular chains then resulting in enhanced crystallinity of the prepared biopolymer film.

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