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Synthesis of graft-copolymer adsorbent through green route and studies on its interactions with chromium (III) through active functional groups: kinetics and improved adsorption supported by SEM-EDX and AFM

J. Kanagaraj *[1a], Rames. C Panda *[1b] and V. Sumathi [2]

[1]CSIR-CLRI, Adyar, Chennai-20, India

[2] Vellore Institute of Technology, Vellore, India

***[1a]** Corresponding author

CSIR- Central Leather Research Institute,

Adyar, Chennai-600020, India.

Ph: 044-24911386 (Off), 044-244530630 (Res),

Fax: 91-044-24911589.

Email: jkraj68@yahoo.co.uk

Abstract

Chromium (III), a heavy metal, contributes potentially towards pollution load, even more than 2000 ppm level in the effluent of many industries. Managing chromium by means of process intensification tools is one of the ways for sustainable development of society and industry. A novel graft co-polymer prepared from collagen hydrolyzate using poly vinyl alcohol (PVA) adsorbent with narrow particle size of 1366 nm has been employed to enhance the uptake of Cr (III) in the tanning process up to 94% using 6% copolymer due to participation of free functional groups of copolymer. Kinetic studies reveal the mechanism of adsorption-diffusion-absorption phenomena confirming Langmuir isotherm. Mathematical models augmented with RSM (supported by DOE) are developed to optimize process. Mechanism of improved absorption has been confirmed by ^{1}HNMR and images of SEM indicating a strong ligand interaction; and by SEM-EDX confirming increase in the rate of adsorption. Images of AFM indicate more amount of chromium adsorbed with increase in the concentration of co-polymer. The increase in intensities of XRD images supports improved absorption of chromium with enhanced interactions with functional groups of collagen-copolymer-chromium complex. CD spectra revealed that the addition of co-polymer increases ellipticity (mdeg value) of the collagen in the cases of 6% and 4% copolymer as compared to the control sample. Application of copolymer in tanning resulted in improved color properties and comparable/ analogous physical strength properties in the leather samples.

Key words: Grafted co-polymer, adsorption of Cr (III), mathematical modeling, adsorption through AFM, XRD and UV studies

Introduction

Industrial wastes containing chromium have adverse effects on environment. Chromium is found in three forms (Cr (0), Cr (III) and Cr (VI)) in waste streams. Among these, Cr (III) and Cr (VI) can be found in polluted streams that cause concern of environmental hazards. [1, 2] Typical industrial waste contains 2000-3000 ppm of chromium (III). Thus, chromium (III) is widely popular as it is used as agents for tanning, steel making etc. It has been found that uptake of chromium in different processes is limited which can be improved by intensification techniques like high-exhaustion, high adsorption etc. A way to increase the adsorption is by means of using high performance auxiliary containing many reactive groups / sites that can adsorb chromium from aqueous environment of process. This motivates the present study. Several researchers have studied improved adsorption techniques of chromium to enhance the performance of the process.

Adsorption of chromium by carboxylic acid groups were suggested by several researchers. Aslan et. al (2014) demonstrated increased absorption of chromium up to 95% in chrome tanning using 5% silk hydrolysate, [3] Liqiang et al. (2014) used amphiphilic acrylic copolymer prepared from lauryl acrylate and acrylic acid as auxiliary chemical in chrome tanning to improve adsorption of Cr. They showed that an increase in acrylic acid during preparation of copolymer increases diffusion of Cr into leather matrix. [4] Gustafsson et al (2014) presented works on Cr (III) adsorption on natural organic matter along with mechanism and modeling. [5] Authors used fleshing hydrolysate (FH) [6] at the level of 2% to improve chrome exhaustion up to 91.5%. In an another attempt nano-particle was prepared from FH- acrylate composite at level of 4%

and found uptake of Cr upto 94%. [7] Chromium exhaustion level of 93% was achieved by application of 1.5% Alutan with 5% BCS during tanning. [8]

Biosorption of trivalent chromium with protonated brown alga ecklonia biomass as a model system [9], chromium adsorption by chitosan Impregnated with microemulsion, [5] horn meal obtained from acid hydrolysis [10] were reported. Gustaffsan presented complexation models to predict chromium (III) solubility in the environment giving scope for utilization of Cr (III). [5] Several polymers and biopolymers are in practice for the effective adsorption of chromium from aqueous environment. Bioadsorption of chromium using cellulose-montmorillonite composite material [11] as the adsorbent by using cellulose-clay composite biosorbent, using *Bacillus pumulus* for the effective removal of chromium at the level of 99.5% has been carried out [12], low molecular soluble polymers supported ultrafiltration for the effective adsorption and separation of hazardous materials like chromium, separation of chromium through sorption by struvite during recovery of phosphorous were discussed. New hydrogels based on substituted anhydride, starch-graft acrylic acid/sodium-montmorllonite superabsorbent, cationic polymer/ bentonite complex as adsorbents, modified collagen hydrolysate, cloisite-g-methacrylic acid copolymer nanocomposites as adsorbents for various applications also have been reported.[13-15]

As the literature reveals that some of the sorbent are very effective in adsorbing toxic chromium (III), the present investigation aims at developing bio based co-polymer matrix to potentially use in the tanning operation in the aqueous environment for effective diffusion through the pores of collagen matrix and fix at multi-point active sites of carboxylic acids in collagen which paves the way for reduction of major amount of Cr

(III) from waste. Thus the objective of this work is to prepare co-polymer, characterize for studying effective adsorption of Cr (III) from the tanning operation in aqueous environment.

Experimental section

Materials

Raw trimmings (collagen wastes) were collected from the tannery division of CLRI, polyvinyl alcohol, acetone, potassium persulfate were purchased from Sigma Aldrich. Skin was procured for adsorption studies during chrome tanning from local vendor.

Preparation of Collagen Hydrolysate (CH)

Collagen waste was weighed, washed with distilled water and minced into small pieces in a mixture. The pieces were taken in a round bottom flask connected to soxhlet extraction unit with heating system for alkaline hydrolysis using 4% sodium hydroxide (based on skin wt) by maintaining the temperature at 80-90°C for a period of 3h. The hydrolysate formed is termed as collagen hydrolysate.

Synthesis of graft copolymer from CH and Poly Vinyl Alcohol (PVA)

Graft co-polymer was prepared using monomers of CH and PVA. 250 ml of distilled water was taken in a three necked round bottom reaction flask attached to magnetic heating system at 90°C with constant stirring. Then 25 g of CH was added and stirred for 60 m with heating to make homogenous mixture. 40 g of polyvinyl alcohol (was dissolved in sufficient amount of ethanol) was added in drops through one of the necks of the flask while initiator, potassium persulfate weighing 1.5 g dissolved in 50 ml of water, was also added in installments through the other neck of the flask. The reaction was allowed to proceed for 3 h with constant heating at 85-90°C with constant stirring. The pH of the resultant product was recorded as 2.0 which was adjusted further to pH of 4 with aqueous solution of sodium bi carbonate. Finally, the co-polymer product was cooled (using desicator) at room temperature and was stored. The characteristic features of the product were analyzed for various parameters using standard methods. The graft copolymer was precipitated from known weight of aliquot of the prepared copolymer using methanol as precipitating solvent. The copolymer was washed several times with water to wash-out unreacted polymers.

Determination of percent grafting and grafting efficiency

A number of experiments were carried out to optimize the polymeric conditions to get desired results. Percent grafting (% PG) and grafting efficiency (% GE), were calculated. After completion of polymerization, the product was extracted using Soxhelt apparatus with methanol to remove the homopolymer. When the extraction time was complete, the sample was carefully transferred into an evaporating dish and the sample was weighed. The percent PG and GE were calculated according/to the formulas given in eqs 1 and 2 by adopting the standard procedure.

$$\text{Percentage grafting (PG)} = \frac{\text{weight of the graft polymer X 100}}{\text{weight of the back bone (polymer)}} \quad (1)$$

$$\text{Grafting efficiency (GE)} = \frac{\text{weight of the grafted copolymer X 100}}{\text{weight of the total polymer (homo + grafted)}} \quad (2)$$

Thermo Gravimetric Analysis (TGA)

The co-polymer sample is subjected to thermal analysis (TGA) using Dupont 2910 DSC instrument with a sample size of about 5-10 mg and heating rate of 10°C per minute in nitrogen atmosphere.

Adsorption of chromium in tanning Process

The pretanned skin (pH of 3) was subjected to traditional chrome tanning process using Basic Chrome Sulfate (BCS) at the level of 8% in a rotating vessel for the duration of 2 h followed by conventional basification using standard procedure. The resultant bath was collected and later recharged in the same process after the addition of copolymer. Three sets of experiment were carried out to the substrate in the same experimental set-up by using the prepared graft co-polymer at the level of 2, 4 and 6% for 90 m in a rotating vessel. Further to that the spent liquors were recharged to the vessel and adsorption reaction was allowed to continue for a period of 60 m in the rotating vessel and then was left for overnight. The adsorption was further continued on the next day for another one hour and aged for 24 h till complete fixation of the Cr (III) to the substrate. The graft copolymer was separated (by Whatman filter paper) and treated with oxalic acid (2%) to dechrome chromium from the copolymer. The resultant solution containing Cr along with chromium in the earlier stream obtained as together was estimated for Cr analysis by quantitative method. The % chrome exhaustion of the sample was found out and verified by spectrophotometrically by UV spectrophotometer.

^{1}H NMR spectra with water suppression using Watergate sequence

0.2ml of sample and 0.4ml of 99.9% D_2O were taken in a standard 5.0mm Wilmad NMR tube. All the samples were prepared in the same proportion. Since the samples contain 90% water and 10% D_2O, obtaining ^{1}H spectrum with standard single pulse sequence was not possible. In order to get well water suppressed ^{1}H spectra, double pulsed field gradient spin echo water gate (DPFGSE) sequence was used to find out the carboxylic acid groups. Before applying this pulse sequence gradient shimming has been done with field gradient control. In all experiments DPFGSE water gate sequence was used to obtain high resolution ^{1}H spectra on JEOL ECA 500MH$_z$ NMR spectrometer.

FT-IR analysis

The samples (controls and experimental) after tanning were collected and dried in the water bath. They were mixed with potassium bromide (1:20; 0.02g of sample with KBr at a final weight of 0.4g) separately. The samples were then ground, desorbed at 60°C for 24 h and pressed to obtain IR-transparent pellets. The FT-IR was first calibrated for background scanning signal against a control sample of pure KBr. FT-IR Spectra of the samples was recorded using an FT-IR spectrum 2000 Perkin-Elmer spectrophotometer within the scanning range of 400-4000 cm^{-1}. Then the experimental sample was also scanned in similar way.

Studies on Kinetics and Optimization

Data collected for adsorption of Cr (III) to the polymer under different temperature, pH, duration and concentration of Cr (III) were used for analysis. Kinetics of adsorption was modeled using Langmuir isotherm. A software program was written in MATLAB (Version 2012a) for simulation and prediction of chromium uptake. Optimal process parameters were found by using optimization tools of RSM supported by DOE. A software program was written for RSM in matlab.

SEM- EDX studies

The control and experimental samples obtained from tanning experiments were dried and made into powder form and then all specimens were then coated with gold using

JEOL JFC-1100E ion-sputtering device. A JEOL JSM-5300 scanning electron microscope was used for the analysis. The micrographs for the sample were obtained by operating the SEM at an accelerating voltage of 20 kV with different lower and higher magnification levels. The sample that showed clear views was presented in the present investigation. Similarly, control and experimental samples were subjected to SEM- EDX studies to assess the effect of absorption of chromium. Both control and experimental samples were gold coated for 3 s and magnified in different magnification ranges. A JOEL JSM 5300 scanning electron microscope with EDX was used to study the experimental samples.

AFM study

For AFM measurements, an Innova apparatus from Veeco Instruments (now Bruker Nano Surfaces Division) was used and visualization was done in tapping mode in air. The feedback signal was optimized for each surface by matching the forward and backward signal of the height channel by varying the proportional and integral gain parameter. Chromium adsorption by the co-polymer was imaged for studies on topography and deflection using standard methods.

UV-vis analysis

Analysis of Cr(III) in spent liquor from experiment and control sample (5ml) after absorption operation were carried out in a UV 1601 spectrophotometer (Shimadzu, Japan) by scanning in the range of 200-800nm to observe the spectral shifts caused by chrome-tanning on experimental samples.

X-ray diffraction

The X-ray diffraction (XRD) studies were carried out using a Japan Science 2200PC X-ray diffractometer. The diffractograms were obtained at 2θ, in the range 2^0 - 10^0 by a Cu-Kα beam (λ=0.1543 nm) monochromated by a nickel filter. Under a scanning speed of 1^0/min and current rating of 40KV and 20mA with X-ray tubes, the morphology of the prepared grafted co-polymer was observed by H-600 transmission electron microscope. bars in Figure.[16]

Circular Dichroism (CD) spectroscopy.

Far-UV CD spectra were recorded on a JASCO-810 automatic recording spectrophotometer at room temperature. A quartz cuvette with a 0.1 cm path length was used. CD spectra were accumulated at a scan rate of 50 nm/min between a wavelength range of 190− 240 nm. 100 µl of experimental and control sample is taken and 3 ml of distilled water is added where as for the polymer sample 0.2 µl of the solution is dissolved in 3 ml distilled water. The protein secondary structure content was determined using the online DICHROWEB server. Each measurement was repeated for three times for which standard deviation from the mean value is represented by error

Color properties

The leather samples after tanning with copolymer were processed into leather and were subjected to study difference in color properties using Gretag Macbeth Spectrolino Spectrophotometer with measurement geometry of $45^o/0^o$. L, a, b, c and H parameters of the measurement were obtained using the standard procedures.

Physical testing

The experimental and control crust leathers samples were performed for various physical tests and the data were obtained as per IULTCS method. Specimens were conditioned at 80±4^{o}C and 65±2%RH. Over a period of 48 hours, physical properties such as tensile strength, % elongation at break, tear strength and grain crack were examined for both experimental and control samples.

Results and discussion

The adsorptive-interaction between the polymer and chromium has been extensively studied in this present investigation and the plausible mechanism has been proposed. The main aim of the work is to develop an efficient adsorbent with high performance in order to improve the uptake of chromium in tanning operations under aqueous environment. Therefore the specific adsorbent has been developed to absorb more chromium.

Characteristics of graft copolymer

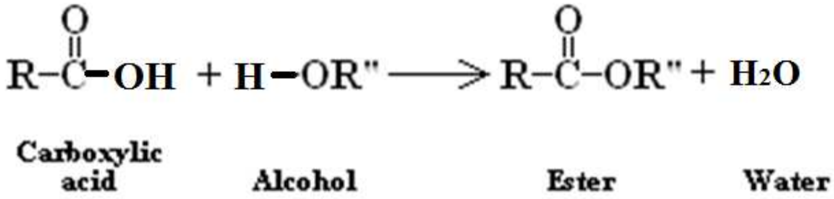
Grafting of copolymer has been carried out using monomers obtained from CH and PVA and has been used as adsorbent in the tanning process which is shown in flow-sheet in Supp. scheme 1. The characteristic properties and structure of the copolymer are given in Supp. Table 1 and Supp. Figure 1. The co-polymer showed particle size of 1366 nm (Figure 1a) which can react with macro-molecules of collagen fibers to bring about better adsorption behavior towards chromium (III) available in the aqueous medium of tanning process. Apart from the particle size the co-polymer has more reactive sites of functional groups that will predominately react with chromium thereby increasing adsorption of the complex. Besides particle size, other important characteristic is molecular weight of the polymer which is found to be 6.0 x10^5 Dalton. The grafting polymerization method generates high molecular weight copolymer with narrow polydispersity index confirming completion of the polymerization reaction for the suitable application as adsorbent of chromium (Supp. Table 1). The polydispersity index of the grafted-co-polymer has been found to be 1.0 based on z-average mean of the particle size distribution while viscosity is found to be 0.85 CP. The co-polymer is readily soluble in aqueous medium as its low-viscosity helps in dispersing the co-polymer in water medium easily promoting better penetration of co-polymer to the porous nature of collagen matrix. Percent solid level of the product is found to be 19.20 which help the co-polymer for dispersing in aqueous medium speeding the diffusion. In the present investigation, co-polymer is added after the chrome tanning process in the same environment which helps to adsorb more chromium from the bath and fixes with active sites of collagen. The structure shows functional groups which plays important role in adsorbing chromium and fixing the active sites of collagen matrix.

Themogravimetric analysis (TGA)

TGA has been carried out to study the decomposition pattern (Figure 1b) and thermal stability of the prepared polymer**.** One can see that there are three stages in the curve. The first stage occurs between 100°C to 254°C indicating about 14 % losses in weight for PVA-grafted-CH copolymer sample. The weight losses in this stage are because of loss in moisture. The second part of the curve represents the maximum weight loss because of the thermal degradation of the sample that happens within temperatures ranging from 300°C to 341°C with weight losses of 52% for the copolymer sample. The third part of decomposition occurred between 400 to 493°C with a weight loss of about 80% which are mostly due to evaporation of volatile compounds. The final stage of decomposition curve is because of formation and evaporation of some volatile compounds from the sample. It can further be found that at around 700°C the char-yield of the product was obtained as 15.86%. The residue is due to charred material consisting of inorganic substances remained as impurities. The copolymer has been synthesized from raw material 'raw trimmings' which contained (i) sodium chloride (preservative) diffused during preservation processes and (ii) some other inorganic ingredients that were used during the synthesis. The char yield has appeared due to the presence of inorganic impurities in the copolymer sample. Thus strong thermal stability property inferred from TGA results indicate that the co-polymer can be applicable in carrying out experiments at elevated temperatures.

Mechanism of graft PVA onto CH

Free carboxylic acid groups from copolymer play main role in adsorbing Cr (III). However, there is a possibility of formation of ester groups due to reaction between carboxylic acid groups and hydroxyl groups of CH and PVA respectively that enables physiochemically to adsorb the Cr from the bath as shown in the scheme 1. Ester helps for the adsorption of Cr through physiochemical changes.



$$R-\overset{O}{\overset{\|}{C}}-OH + H-OR'' \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR'' + H_2O$$

Scheme 1. Stoichiometric reaction for formation of ester by grafting PVA onto CH

Adsorption study in chrome tanning process with graft co-polymer

The skins/pelts that are ready for chrome tanning (pickled skin pH of 3.0 is used) were taken. Traditional chrome tanning was carried out using BCS at the level of 8% and is agitated in a mechanical drum for about 180 m for the completion of tanning. With the same substrate, co-polymer at various levels 2, 4 and 6% were treated and are agitated in a mechanical drum for about 60 m. The effect of pH on chrome (III) uptake was studied. The results are presented in Figure 2. It has been found from the Figure. 2a that pH at the level of 4 gave maximum chrome uptake up-to the level of 92.18% at room temperature of 37°C. The reaction between the complex and collagen is a kinetically controlled process. [17,18] The effect of temperature on the enhancement has been studied. It is seen from the Figure. 2b that the maximum exhaustion of chromium is found be 94.20% at the temperature of 42°C. The reason may be, higher the temperature faster the chrome-complex reaction with collagen. The effect of duration of chrome tanning on the extent of exhaustion in Cr (III) uptake by the substrate is shown in Figure 2c. The exhaustion increases with the duration of tanning. The exhaustion was high at 5 h showing 93.70% while the curve tends to decrease after this duration. The characteristics of waste water from chrome tanning are presented in Table 1. It can be found from this table that the chromium content is 450 ppm while, BOD, 850 ppm, COD, 2560 ppm, suspended solids, 680 ppm. The contribution of BOD is mainly due to the biological/organic materials present in the bath mainly loosened protein material in the tanning process and unspent copolymer mainly the collagen hydrolysate. The contribution towards BOD by the later is negligible. Chromium and other chemicals used in the tanning process such as sodium formate and bicarbonate for the basification process in tanning may contribute majority of COD. There is a drastic reduction of chromium content in the waste water due to increased absorption of chromium. Ammonium nitrogen and TKN is found to be 80 and 90 ppm respectively which may be due to the presence of collagenous hydrolysate and soluble proteins/extractable proteins in the tanning process. The chlorides contributes to 25000ppm which may be due to the neutral salts present in the tanning agent, chlorides used in earlier process namely pickling process and the salts used in basification steps of tanning process itself. The contribution of sulphates is 12000 ppm which may be due to tanning salts and the alkali used in basification process.

Use of silk-hydrolysate in chrome tanning increased adsorption capacity from 2.56% to 3.47% as Cr_2O_3. [3] Novel pretanning agent was used in tanning to increase exhaustion from 70.6% to 96.5% as compared to 94.2% by application of 6% copolymer in the present work. [27] Application of FH, and nano-particle dispersion gave chrome adsorption at the level of 91.5 % (by the application of 2%) and 94% (using NPD at the level of 4%).[6,7] Application of Alutan – BCS showed chrome adsorption up to level of 93%. Application of novel cross linking agent in the chrome tanning gave chrome exhaustion at the level of 96%.[8] (by applying 6% cross linking agent). However, the method suffers from pollution from heavy metals and is not favorable.

^{1}H NMR studies for the mechanism of adsorption

^{1}H NMR studies are very important in investigating functional groups responsible for adsorption of Cr in the chrome tanning process revealing the mechanism of adsorption. Two samples, one co-polymer treated at the level of 2% in chrome tanning and the other pure co-polymer were considered for ^{1}HNMR studies. The results of the ^{1}H NMR investigations are presented in Figure 3a and Figure 3b, showed reduced peaks at 8.433 ppm due to presence of free COOH. It is evident from the investigation that increased absorption of Cr has been possible due to the presence of free carboxylic acid functional sites.

FT-IR investigation

Three different FTIR spectra have been undertaken for identifying functional groups of Protein, PVA and copolymer. The results are presented in supporting Figures 4 (a-c). The FTIR spectra of protein shows peak at 3465 cm^{-1} indicating protein containing OH and NH groups. Peak at 1638 cm^{-1} represents presence of protein of amide-I. FTIR spectra of PVA sample reveals presence of OH groups corresponding to peaks 3625, 3605, 3644 cm^{-1}. The peak at 1644 cm^{-1} indicates presence of amide –I for N-H stretching in FTIR of PVA. FTIR spectra of copolymer show peaks at 3625 and 2938 indicating presence of OH groups. Moreover, peak at 1555 cm^{-1} represents amide-II and 1644 cm^{-1} represents ester groups.

The experimental samples prepared by addition of copolymer at the level of 2, 4 and 6% during tanning are also subjected to FT-IR study (Figure 4 (d-f)). It can be observed from all figures that a broad and wide spectrum appearing at 3386 cm^{-1} for the experimental samples are due to presence of stretching frequency of the O–H groups (hydrogen bond) indicating protein containing OH and NH groups. The peak presented in all the experimental samples represents presence of amide I. The amide group provides stability by means of hydrogen bonding and hydrophobic interactions with the collagen.

Kinetics of Chromium (III) uptake

Mathematical models are necessary for studying optimization of raw materials, operating parameters, scale-up studies and to understand mechanism of adsorption-diffusion-absorption phenomena. Therefore, in this section, mathematical model has been formulated to study kinetics and optimization of absorption of Cr (III) by leather. It has been noticed from design of experiments (DOE) that Cr (III) exhaustion (output) is influenced mostly by pH, duration and temperature. Cr (III)-Copolymer Complex (CPC) molecules being so large, establishes linkages/ binding with basic groups of polymer matrix of synthetic co-polymer at a pH about 4-7. Cr (III) ions also bind/combine with functional groups present in the collagen matrix.[19] There exist ionic-interactions due to dipole, hydrogen bond or dispersion in the binding form. With the addition of Cr (III), molecules of co-polymer complex get distributed into media and get adsorbed /transported into collagen matrix. Slowly they get diffused through pores of leather and get absorbed or fixed through binding/linkages. Equilibrium reaches when absorption balances desorption of (CPC) molecules. The relation between concentration of Cr (III) in bath and in absorbed state is governed by isotherm. Though diffusion is a fast process fixation completes below iso-electric point of pH.[20] Absorption and kinetics of CPC uptake have been explained by many researchers [41],[42]. A continuous formation of monolayer of chrome-polymer complex (CPC) on surface of flesh side (inner side of leather) is assumed here initially. In the two stage process of uptake, CPC molecules reach to collagen and adsorb through their reactive sites fast followed by penetration through pores and micro-pores by diffusion controlled process making the rate sluggish.

Mass Transfer model

Let’s think of a mass of leather (weight m_L gm, porosity, ε and volume V lit) be dipped in an aqueous CPC solution of concentration, C_0 (g/l) in a stirred tank with a constant flow rate F_0 (lpm). With progress of time (t min) concentration of CPC in bath gets depleted (c g/l) as CPC molecules proceed towards collagen, gets adsorbed and diffused through pores inside leather matrix (concentration, q mg/g). This absorbed concentration slowly increases and reaches to equilibrium (qe). Considering mass balance inside the tank,

$$\frac{q-q_e}{q_0-q_e}=\frac{F_0}{V\left\{\varepsilon+(1-\varepsilon)\rho_L\dfrac{q}{c_0}\right\}}\int_0^\infty\frac{c_0-c}{c_0}dt \qquad \textbf{(1)}$$

Where ρ_L is the density of liquid in the tank. When equilibrium between absorption and desorption is reached process attains steady state and inlet flow rate of CPC becomes equal to outlet flow rate of CPC in the tank.

$$\frac{q-q_e}{q_0-q_e}=\frac{F_0}{V\left\{\varepsilon+(1-\varepsilon)\rho_L\dfrac{q}{c_0}\right\}}\int_0^\infty\frac{c_0-c}{c_0}dt$$

the process of CPC absorption can be given by following mass balance

$$q-q_e=\frac{(c_0-c_e)v_0}{m_L} \qquad (2)$$

where suffix 0 represents initial condition of respective variables.

Eq (1) can be solved to get q or c versus time for a specific span of reaction time provided the equilibrium value of q_e is known. To find out q_e (or to establish a relation between amount adsorbed and concentration of remaining CPC in bath) one needs to explore the isotherm mechanism and kinetics behind CPC absorption.

Kinetic model

The rate of absorption of CPC inside the porous leather can be represented by pseudo 2nd order kinetics as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \qquad (3)$$

With initial conditions as

$$at \quad t = 0 \quad , \quad q = 0$$

$$at \quad t = t_f \quad , \quad q = q_e$$

simplifying, eq(3) we get

$$\frac{dq}{(q_e - q)^2} = k_2 dt$$

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Eq (4) provides information on the reactions at the 1st stage of CPC uptake. In this equation qe can be obtained from Langmuir isotherm or Freundlich isotherm as

$$q_e = \frac{q_m k_2 c_e}{1 + k_2 c_e} \qquad \text{Langmuir Isotherm} \qquad (5A)$$

$$\ln(q_e) = \ln(k_2) + \frac{1}{n} \ln(c_e) \qquad \text{Freundlich Isotherm} \qquad (5B)$$

and c_e is related to q_e by

$$c_e = c_0 - \frac{q_e m_L}{V_0} \qquad (6)$$

In case of Langmuir isotherm, monolayer of adsorption should be observed.

Model validation

CPC solution is prepared in three different concentrations 2%, 4% and 6%. About 800 gm of skin is dipped into 600 ml of CPC solution. The pH of the solution was kept at different levels ranging from 3-5 in different sets of experiments and temperature was also varied from 35-50°C in different sets of experiments. Each experiment was carried out under fixed operating conditions and uptake was calculated. CPC uptake is plotted against time in Figure 2. Figure 2a. plots absorption of CPC (q) with changes in pH whereas Figure1c shows a graph of absorption of CPC (q) against time where q represents mg of CPC absorbed per gm of leather. It can be seen that uptake increases with concentration of CPC reaching a maximum of 93% at pH=4 and then declines at higher pH (confirming that the process is favorable between pH 3 to 5). At 42°C the exhaustion (Figure 2b) of chrome is about 93% showing optimal value. When uptake was plotted against time, it was found that uptake increases with time attains about 94% after 5 h. Figure 5 shows a plot of (t/q) against time. Theoretically obtained (t/q) from Eq(4) has been plotted and compared with experimental values. A value of R^2 = 0.93 has been obtained indicating quite good agreement between theoretical and experimental values that validates the model. Value of adsorption constant is noted as K_2 = 0.1006. Thus it can be interpreted that CPC absorption by leather is better represented by Langmuir isotherm.

Optimization studies using response surface methodology

Several traditional methods are available to find out values of optimal process parameters. These methods find one parameter in a single run. Processes which are affected by many parameters can be optimized using response surface methodology

(RSM). Statistical optimizations supported by design of experiments screens key factors from multi-dimensional systems to evaluate optimal operating conditions of diffusion come reaction problem. There are some reports on application of RSM in CPC degradation in waste stream. This type of study in applying multi-factorial design for screening/ sorting variables and finding optimal there from for adsorption-diffusion-reaction process is being reported for first time in application of 'chrome uptake' by leather. Chrome uptake has been found to be influenced by initial BCS concentration, temperature, pH, duration parameters.

The main objective of RSM is to find levels of p levels of design factor variables that optimize the CPC uptake over an experimental region. This method is used to formulate a performance function consisting of dependent variables which is needed to be optimized. A Box-Behnken design with three variables and three levels (1, 0, -1) is designed to generate 15 experimental conditions using pH, temperature and duration as variables. Total number of experiments becomes $2^K + 2K + n_0$ with k being the number of independent variables (3) and n_0 be the number of repetition of the experiment (1).

The data-file containing experimentally observed values of CPC uptake due to change in pH, temperature and duration of reaction is normalized and is used as input data file to RSM program written in MATLAB version 2012a. Result of optimization is shown in Figure 2. Uptake decreases at higher pH but increases at higher temperature. It is favorable between pH 3-5 and at higher temperatures (37-45^{o}C) as is evident from Figure 8a. Temperature plays a significant role in increasing the uptake rate by enhancing pore diffusion process. Response surface (Figure 5(a-c)) shows variation of uptake for changes in duration and temperature. It can be seen from this Figure that uptake increases with increases in both the variables. Optimum temperature is found to be 42^{o}C for maximum absorption. Optimal surface can clearly be observed in case of variation of uptake with respect to duration of reaction and pH of tank or CPC. Uptake is favorable at optimal pH 5 and optimal duration 5 h.

Contour plots (Figure 5(d-f)) show change or variation of uptake due to changes in variables while rate of change of other variable is hold constant. Figure indicates that under constant slope of durations, uptake increases with rise in temperatures. With constant slope of pH, uptake rate increases with increase in temperature and duration as is revealed from Figure. At a pH of 4 and with long duration of immersion of leather piece in the CPC bath, (under constant temperature) the uptake becomes high as can be noticed from Figure 1e. These profiles demonstrate the safe operational strategies for designing and operating the reactor for CPC-uptake of leather.

Researchers have studied adsorption and improved exhaustion of chromium (III) into the collagen matrix in tanning process. During chrome tanning, chromium (III) in the form of BCS is added for penetration/ diffusion through the pores of skin. Predominantly, Cr (III) is cationic in nature and mostly dimer species are present in BCS. This chromium (III) is attracted towards the carboxylic acid sites of collagen. Cr (III) gets fixed with the carboxylic acid groups of collagen comprising of aspartic acid, glutamic acid etc by means of co-ordinate covalent linkage which is stronger, irreversible bond and brings about highest hydrothermal stability in the tanning process. If tanning is carried out in anionic conditions the basic amino acids such as lysine and arginine play important role in fixation of Cr (III). All these amino acid residues can act as hydrogen bond donors and acceptors.

Plausible mechanisms for the improved adsorption of chromium by using copolymer

In the present investigation, the grafted co-polymer that is employed for tanning process after the fixation of Cr (III) plays a major role in inviting / attracting more amount of Cr (III) from aqueous medium to the collage matrix and thereby more adsorption takes place finally resulting in higher exhaustion of chromium in the tanning process. The improved adsorption leading to high exhaustion takes place in three possible reactions.

Firstly, the free carboxylic groups present in the copolymer play important role in adsorbing Cr (Figure 6). The free carboxylic acids of copolymer may form hydrogen bonding at multipoint in providing additional adsorption and exhaustion to the complex. The interaction between CPC helps to hold more amount of the chromium with co-polymer and favor COO-Cr-Copolymer-Cr type of cross links. The second reason may be due to functional hydroxyl groups of PVA that forms H-bonding with carboxyl groups of collagen. PVA used here generate more saponified groups of -Ol- (OH groups) that can generate more functional groups responsible for improved dyeing process.

Thirdly, the ester groups from copolymer along with free functional carboxylic acid groups play role in adsorbing Cr (Table 2).

Esterification occurs in acidic conditions due to protonation of amino and carboxyl groups. The carboxyl groups on polymer side chains and unesterified hydroxyl groups of PVA can react with active groups of collagen via hydrogen / covalent bonds during tanning, and thereby increases absorption of Cr.

In addition to these, the ester groups form good masking for chrome complexes. Masking is the term used to slow the reactivity of chrome complexes, distributes Cr uniformly throughout the substrate mainly to satisfy all the reactive groups of collagen, thereby higher absorption of chrome is achieved. Masking reduces the astringency of chrome complexes thereby reduces the risk of case hardening and increases the amount of fixation of chromium. The ester plays the role of masking and helps for the higher percentage of chromium absorption in the tanning processes.

Several researchers [3-8] suggested that main reason for the improved adsorption / exhaustion of chromium (III) may be due to the presence of additional carboxylic acid sites present in the complex matrix. [21-31] Use of fleshing hydrolysate and modified fleshing hydrolysate [6, 7] that contains reactive groups of aldehyde, [23] nano particle dispersion in tanning process [24-26], oxazolidine derivatives [27], compound prepared from chromium-keratin [24], application of acid protease in tanning [28] to enhance the uptake of chromium has been suggested. The mechanism of binding chromium to the collagen matrix has been proposed by many researchers.[29-32] Several adsorbents prepared from different sources were developed for various applications.[33-42] In a separate study comprising of raw fleshings and complexed with iron is used for removal of other forms of chromium,[37] a homogeneous polymer prepared from cationic poly (2-aminoethyl methacrylate hydrochloride) with oppositely charged poly(2-carboxyethyl acrylate) as an adsorbent from protein solutions, akovite−alumino silicate nano-composite adsorbent for Cr3+ ions from aqueous solutions is reported.[39]

SEM and SEM-EDX Analyses

SEM analyses were carried out to capture morphology of the polymer, co-ordinated complex and chromium impregnated complex at different magnification levels. There are two types of structure visible in the image (i) fibrous and (ii) small crystalline grains. While the former is for CH the later is due to PVA grains forming layers.

Experimental sample obtained by treating co-polymer (at various concentrations such as 2, 4 and 6%) were also subjected to SEM analyses and the SEM figures are presented in Supp. Figure 2. It can be seen from the images (921X20 μm) that there exist two types of structures, one grain structure is impregnated on fibrous layers of co-polymer confirming more amount of Cr absorbed on the surface. This indicates most of the active sites are occupied by Cr leaving almost no bright white-fibrous layers. It can also be observed from the images (958 X 20 μm, 860 X 20 μm) of the samples that have been treated with 4 & 6%, that most of the active sites of co-polymer are occupied by Cr (as seen by globular grain structure embedded in the fibrous structure of the co-polymer in the image) leaving almost no-empty fibrous structures of the co-polymer. The amounts of Cr adsorbed by different samples have been quantitatively given in SEM-EDX. The results of the SEM-EDX investigations are presented in Figure 7.

It is evidenced from the images of SEM-EDX that with increase in concentration of co-polymer, the amount of absorption of Cr increases. In case of 2% copolymer sample, weight % of Cr is 4.48 while atomic % is 2.34 indicating relatively higher amount of Cr as present in the sample confirming relatively lower amount of Cr had been absorbed in the co-ordinated complex. Experiment carried out with the help of 4% and 6% samples showed weight % of Cr by 5.24, 2.31 while atomic % by 1.67, 0.75 respectively (relatively less amount of the Cr present in the sample). It is evident from the SEM-EDX that increase in the amount of co-polymer increases the rate of adsorption, thereby; more Cr has been taken up by the leather.

AFM analysis

AFM has been carried out to capture high resolution imaging of graft copolymer and collagen bound chromium-polymer complexes. AFM provides topographical information of the sample with nano scale resolutions. One pure polymer sample and three experimental samples (2%, 4% and 6%) with different resolution as 4μm, 8 μm, 25 μm and 810 nm are prepared by to facilitate AFM study. Though the resolutions were chosen at different scales, 25 μm scales was selected for optimal visualization of the image hence the particular resolution was chosen for the detailed results, interpretation and discussion. In order to study the effect of graft copolymer for enhanced adsorption and to study the hydrophobicity increasing concentration of grafted copolymer was chosen for the AFM study.

Topography and deflection of the grafted-co-polymer sample and for experimental samples are obtained from AFM and are shown in Figure 8. The image shows surfaces such as PVA and CH with clear distinguished features. The surface fits show topography of the height image. In this image, two different morphological structures can be observed as bigger and smaller particles (almost similar to globular structure). Bigger molecular chunks are due to polyvinyl alcohol (PVA) while smaller molecular colonies are attributed to CH those adhered to one another with almost no spaces between two monomers. The deflection image shows one linear thread or fiber like structure which may be due to CH fiber. It is evident from the image that the co-polymer is formed with various functional groups comprising mostly of carboxylic acid sites. The CH provides more colonies with more number of atoms and gives lack in stiffness. While, bigger molecules of PVA give stiffness in structure. The darker gaps in right top corner of topography are due to non-uniformity of spread of bigger molecules of PVA. The non-uniformity inherited by two monomers CH and PVA that yielded co-polymer of varying sizes increased absorption phenomena during chrome tanning. This appearance is typical in the adsorption of fibronectin on titanium surfaces.[39]

The line graph of the surface topography has been provided with mean fit showing uniform distribution of the polymer sample (Supp. Fig 3). Similarly the line graphs representing surface roughness of deflection image shows regular distribution of the sample around the mean fit. Moreover the isometric view of deflection sample (3d) can be observed in a scale of 25 μm/ 80.6 m showing scattered peaks indicating provision for adsorbing more Cr (III) through the available spaces or trench (Figure 9).

The experimental sample that had been treated with 2% copolymer in the chrome tanning process was considered for adsorption study. The related AFM image has been shown in Figure 8. The topography with scan forward mode of tip of AFM shows darker region in the middle, indicating the presence of adequate amount of chromium compared to almost non visible copolymer in the sample. The reason may be attributed to insufficient amount of copolymer that has been used to adsorb chromium in the experimental condition. It can be assumed that the amount of co-polymer used in the experiment is fully adsorbed by collagen matrix hence not visible/captured in the AFM image. The faded lighter portions along the sides represent the available/ scope for possible more adsorption. The line graph representing the topography shows uniform and smoother spread of the sample around the mean fit.

In order to increase adsorption of Cr, next AFM study was carried out collecting sample from experiments conducted using 4% copolymer in the chrome tanning process. The AFM images from the adsorption study have been presented in Figure 8. The topography with scan forward mode of tip of AFM shows slightly darker band (as compared to previous sample with 2% co-polymer) in the middle, indicating the presence of comparatively lesser amount of remaining chromium. The reason may be due to non-availability of free functional groups especially carboxylic sites present in the co-polymer for adsorbing Cr in the process. It can be inferred from the image that no-visualization of the co-polymer shows better/more absorption of Cr by collagen matrix.

The AFM image of sample with 6% co-polymer from experimental conditions is presented in Figure 8. The image gives clear evidence of maximum adsorption of Cr compared to the previous experiments. The deflection image also shows almost no Cr left in the bath. In this image, there are two types of particles seen; one is bigger globular and other is long threaded or linear; first one represents copolymer and second represents CH. It is confirmed from the image almost maximum adsorption of Cr has been taken place and no Cr is seen in the image of deflection sample. This result agrees with 94% of adsorption of Cr as revealed by kinetic study. As the polymer has adsorbed more Cr, the height of deflection image (Figure 9) is also more than the previous similar images of earlier samples. Almost absence of darker spots/gaps in the deflection/ topography indicates complete binding of Cr by functional groups of co-polymer hence improving efficiency of absorption. It can also be inferred that increase in surface roughness has resulted due to increase in concentration and hydrophobicity of the grafted co-polymer.

UV analyses

Uv analyses is very important tool to measure the rate of adsorption of chromium by using the copolymer in the experimental samples The results obtained during experiments are presented in Figure 10a. The rate of adsorption of chromium by the copolymer showed increased chromium exhaustion that was confirmed using UV-vis spectroscopy at the peak intensity of of 200-800 cm^{-1} wavenumber in the tanning process. UV results show uniform increase in adsorption rate of Cr (III) in the experimental samples by the application of copolymer at 2, 4, 6% level in comparison with the lowest adsorption of the controlled samples. The maximum adsorption of Cr (III) was found to be in the experimental sample carried out with the application of copolymer at 6% level. The absorption unit observed for the sample is 2.4 a.u. Similarly, the rate of adsorption of Cr (III) for the experimental sample carried out with application of copolymer at 2 and 4% showed adsorption rate of 2.8 and 3 a.u respectively. The control sample (without application of co-polymer) showed adsorption rate of 3.8 a.u. Hence the UV results indicate that enhanced adsorption of Cr (III) by the co-polymer is due to strong interactions between the Cr (III) and -COO- groups of copolymer along with ester and the charged nature of collagen matrix that lead to improved adsorption of Cr (III) in the process.

X RD analysis

The XRD analyses give important information on morphology and distance between important functional groups (atomic distance between two molecules) of the co-polymer (Figure 10b). The analyses carried out for the experimental and control samples give valid information on the adsorption of chromium with the copolymer. Figure shows XRD pattern for pure graft copolymer synthesized from collagen hydrolysate and experimental sample of this treated copolymer at various level of 2, 4 and 6% in the chrome tanning process. Two broad peaks and relatively two small peaks are visible at $2\theta = 18^{o}$, 22^{o}, 32^{o} and 40^{o} and then flattens. These peaks were similar to the collagen extracted from the scrap leather of the pure collagen.[41] The experimental sample showed presence of characteristic diffraction peaks of chromium adsorbed copolymer sample at $2\theta = 10^{o}$- 80^{o}. Absence these of peaks in the experimental except at 32^{o} reveals the functional groups have undergone reactive absorption of Cr (III) into the copolymer and with the reactive groups of collagen in the amorphous region. Moreover, the compatibility between the reactants was very good and the longer chains are converted to reduce molecular order due to the grafted copolymer on the collagen. The intensity of peaks in adsorbed polymer of the experimental sample increases sharply indicating the displacement of functional groups of copolymer, chromium (III) and collagen matrix by large angles and the reduction in crystalline nature of amide group to the appreciable level. These results further suggests that the aggregation of the amide groups after absorption of chromium (on copolymer), tend to increase in the area of amorphous region which is due to the deposition of chromium in the polymer and the interaction between chromium and the active groups of the polymer. The increase in intensities of XRD images indicates increased absorption of chromium through interactions with functional groups in the collagen-copolymer-chromium complex.

Circular Dichroism (CD) analysis

CD utilizes the differential absorption of circular polarized light in an asymmetrical environment to assess structure. The amide bonds of a protein in highly ordered regions such as helices and beta sheets have specific optical activity due to orientation. CD has commonly been employed as a technique to characterize the helical content of collagen. The helical nature of collagen is responsible for restoration of important structural properties of leather. CD has been used to assess the susceptibility of collagen to ultraviolet light based on loss of helicity, to confirm the presence of collagen helical content for collagen-like peptides or converted into other secondary structures.

CD was used to examine helical content as a function of heat denaturation (temperature melts), as a reflection of structure and chemistry. For both experimental and control samples, the pure copolymer of the helical content of the collagen solutions and the films was confirmed by CD. The results of the CD investigations are presented in Figure 11. The CD curve for the native (nondenatured) collagen shows the expected profile for a helical collagen molecule including maxima and minima at 221 and 197 nm, respectively and a significant decrease in the mdeg value at positive peak at 221 nm representing denatured state of collagen sample.

The pure polymer sample shows almost straight line indicating most of the helical collagen molecule in collagen hydrolysate that has been used to prepare co-polymer has been converted into random coils or some other secondary protein losing its original helical structures. These secondary structure may be derivatives of broken poly peptide chains of collagen into C=O and –N-H groups.

Increase in mdeg value represents α-helicity due to presence of active sites in co-polymer that may adsorb / interact with helices over β- sheet structure. Sample with 2% copolymer on CH showed negative absorption profile between 208 nm and 222 nm (peak at 214nm) which is due to the π → π* transition of carbonyl groups in polypeptide chains. The figure shows peak at 208 nm in case of 6% copolymer treated sample whereas peak at 210nm is attributed to sample with addition of 4% co-polymer in the tanning. The control sample showed lesser mdeg (18) values compared to that of 4% (38) and 6% (60) samples. The presence of co-polymer results in increase of ellipticity (mdeg value) of the collagen in the cases of 6% and 4% polymer with CH compared to the control sample.

Color measurement study

The leather produced after improved tanning operation using the copolymer was studied for the color measurement property by using CIELAB system. The results are presented in Table 3. L, a, b, c are color co-ordinates and h is hue. ∆a, ∆b , ∆c are red-green, yellow-blue color differences and chromaticity differences respectively. Three experimental samples produced by using the copolymer at the level of 2,4 and 6%, show proportionally increasing trend of darker color in comparison with control samples as evident from L values of the various samples. The experimental samples also show relatively lower ∆a and ∆b value which is due to the presence of more green and less yellow component when compared with the control sample. The chromaticity and hue difference is also lower in the experimental sample compared to the control samples. The overall color differences (ΔE) for the experimental leather samples produced from the treatment of copolymer at the level of 2, 4 and 6%, show 0.48, 14.44, 16.06 values and this is due to increased uptake of dye which is responsible for carboxylic reactive site present in the copolymer sample.

Physical strength properties of leather

The leathers obtained from the improved chrome exhaustion systems were analyzed for the performance in terms of strength properties by standard physical testing methods and are presented in Table 4 along with standard deviation. The leathers obtained from the various experiments (copolymer offer at the level of 2, 4 and 6%) show analogous strength values with that of control leathers, comparable to Bureau of Indian Standard norms. Physical strength properties such as tensile strength, elongation at break, tear strength, load at grain crack and distension at grain crack were comparable to the control leather with repetition of 5 times for obtaining the standard results. Similar results were reported by other researchers.

Conclusion

A novel graft co-polymer from collagen hydrolyzate and poly vinyl alcohol (PVA) is prepared to be used as an adsorbent with narrow particle size of 1366 nm. It has been applied for the adsorption of Cr (III) that resulted in 94% absorption which was further supported by kinetics and associated modeling explaining adsorption-diffusion-reaction mechanism for improved absorption of Cr (III). It has been found that the absorption is supported by Langmuir isotherm and an adsorption constant of 0.1006 was found to fit the model. The co- polymer having carboxylic acid active sites plays important role in enhancing the adsorption of Cr (III) in the process. Ester groups also play minor role in stabilizing the adsorption phenomena. TGA and FTIR analyses showed that the copolymer exhibit better thermal stability and characteristic peak of –OH stretching and NH bending confirming the presence of amide. A plausible mechanism of formation of Cr-Co-Polymer-collagen complex has been suggested for the improved adsorption. SEM confirmed improved uptake of chromium. Quantitative increase in absorption was observed in SEM-EDX results with application of copolymer at the level of 4% and 6% showed weight % of Cr by 5.24, 2.31 while atomic % by 1.67, 0.75 respectively indicating higher rate of Cr adsorption in the leather matrix. The AFM study showed clear topographical view indicating mechanism of Cr adsorption using grafted-co-polymer during chrome absorption process. The images captured from AFM of different samples have also provided evidences on increased hydrophobicity and softness behavior of Cr-Co-Polymer complexes. A UV analysis shows systematic improvement of the absorption of Cr (III) through active functional groups as seen from intensity and absorbance graph by the application of 6% copolymer as evidenced from relatively lesser absorbance of 2.4 (au) in the sample. CD spectral findings also showed increased ellipticity (mdeg value) of the collagen in the cases of 6% and 4% copolymer treated samples. Application of copolymer in tanning resulted in final leather which showed improved color measurement and comparable / analogous physical strength properties. The developed high performance adsorbent provides not only a greener process but also helps in minimizing amount of solid wastes especially collagenous waste.

Supporting Information

Supporting Scheme 1, Supporting Table 1, representing characteristics of grafted copolymer, Supporting Figure 1 representing the structure of copolymer, Supporting

Figure 2, SEM analysis, Supporting Figure 3, indicating topography and mean fit of the experimental samples obtained from AFM study have been provided in supporting information section.

Notes

The author declares no competing financial interest.

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Table 1 Characteristics of the waste water from chrome tanning process

Parameter	Values (ppm)
Total Chromium as Cr	450
BOD	850
COD	2560
Suspended Solids	680
Ammonium nitrogen	80
Total kjeldahl nitrogen (TKN)	90
chlorides	25000
sulphates	12000
pH	3.2

Table 2 Percentage of grafting and grafting efficiency of graft PVA on CH

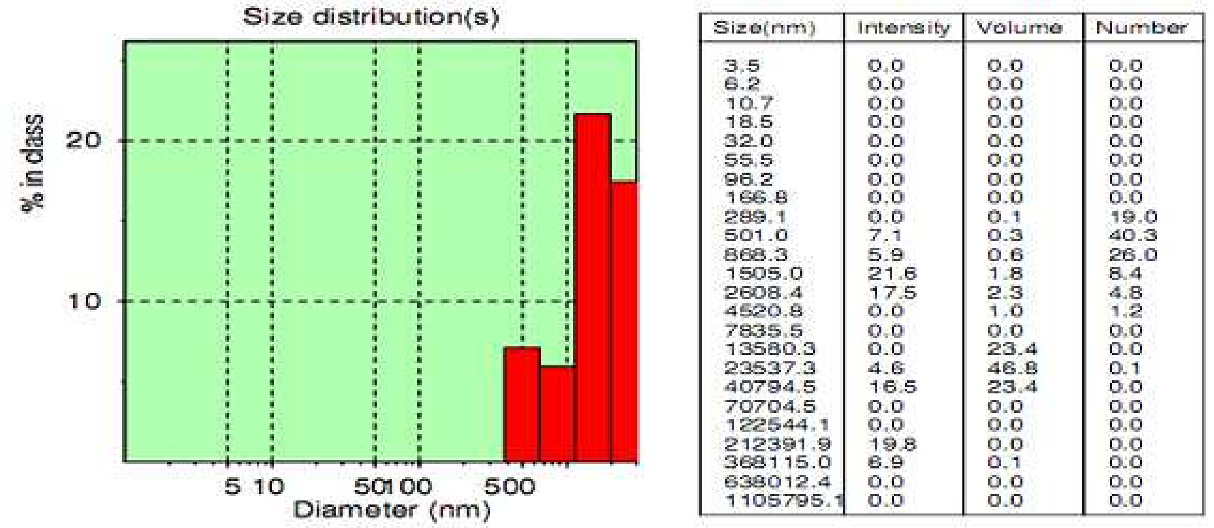
Total polymer (g)	Wt. of graft	Percentage grafting (PG)	Percentage Grafting Efficiency (PGE)
66.5	6.0	60.0	92.3

Table 3 Color measurement study for the leather

Color measurement study						ΔE : Overall color differences				
Samples	L	a	b	c	H	Samples	Δ L	Δa	Δb	ΔE
Copolymer-6%	42.02	7.15	6.31	10.00	41.58	Copolymer-6%	-3.91	-1.97	2.14	16.06,
Copolymer-4%	42.52	7.68	6.10	9.817	41.22	Copolymer-4%	-3.42	-1.44	-2.35	14.44
Copolymer-2%	44.883	8.723	7.562	11.544	43.800					
Control 1	45.94	9.13	8.45	12.44	44.17	Copolymer-2%	-1.06	-0.41	-0.89	0.48

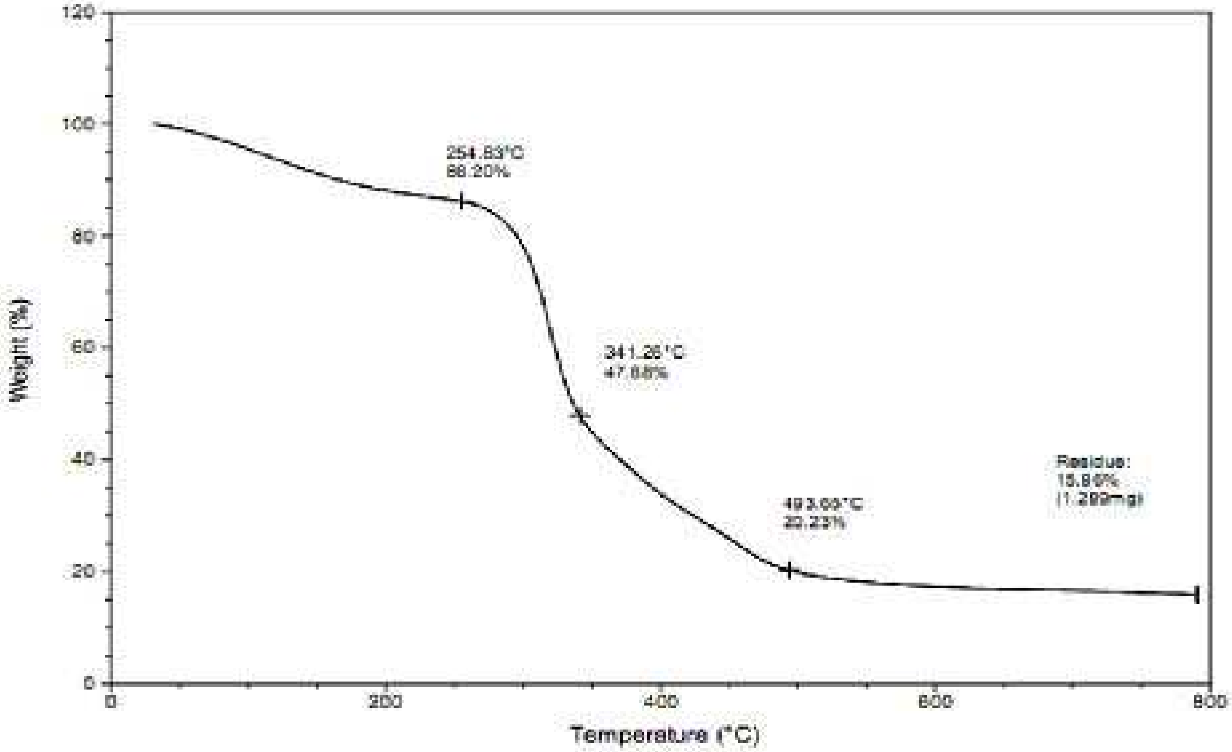
Table 4 Physical strength properties of the leather

Parameters	Copolyemr-2%	Copolyemr-4%	Copolyemr-6%	Control
Tensile strength (kg/cm^2)	224±2.0	242±4.0	260±4.0	220 ±4.0
Elongation at break (%)	52±0.5	55±1.0	58±2.0	55±1.0
Tear strength (kg/cm)	48±1.0	50±1.0	54±3.0	50±1.0
Load at grain crack (kg)	36±0.8	38±1.0	40±1.0	40±1.0
Distension at grain crack (mm)	10±0.1	12±0.2	16±0.2	14±0.1



Size(nm)	Intensity	Volume	Number
3.5	0.0	0.0	0.0
6.2	0.0	0.0	0.0
10.7	0.0	0.0	0.0
18.5	0.0	0.0	0.0
32.0	0.0	0.0	0.0
55.5	0.0	0.0	0.0
96.2	0.0	0.0	0.0
166.8	0.0	0.0	0.0
289.1	0.0	0.1	19.0
501.0	7.1	0.3	40.3
868.3	5.9	0.6	26.0
1505.0	21.6	1.8	8.4
2608.4	17.5	2.3	4.8
4520.8	0.0	1.0	1.2
7835.5	0.0	0.0	0.0
13580.3	0.0	23.4	0.0
23537.3	4.6	46.8	0.1
40794.5	16.5	23.4	0.0
70704.5	0.0	0.0	0.0
122544.1	0.0	0.0	0.0
212391.9	19.8	0.0	0.0
368115.0	6.9	0.1	0.0
638012.4	0.0	0.0	0.0
1105795.1	0.0	0.0	0.0

a)



b)

Fig. 1 a) Particle size of the grafted copolymer, b) TGA analysis

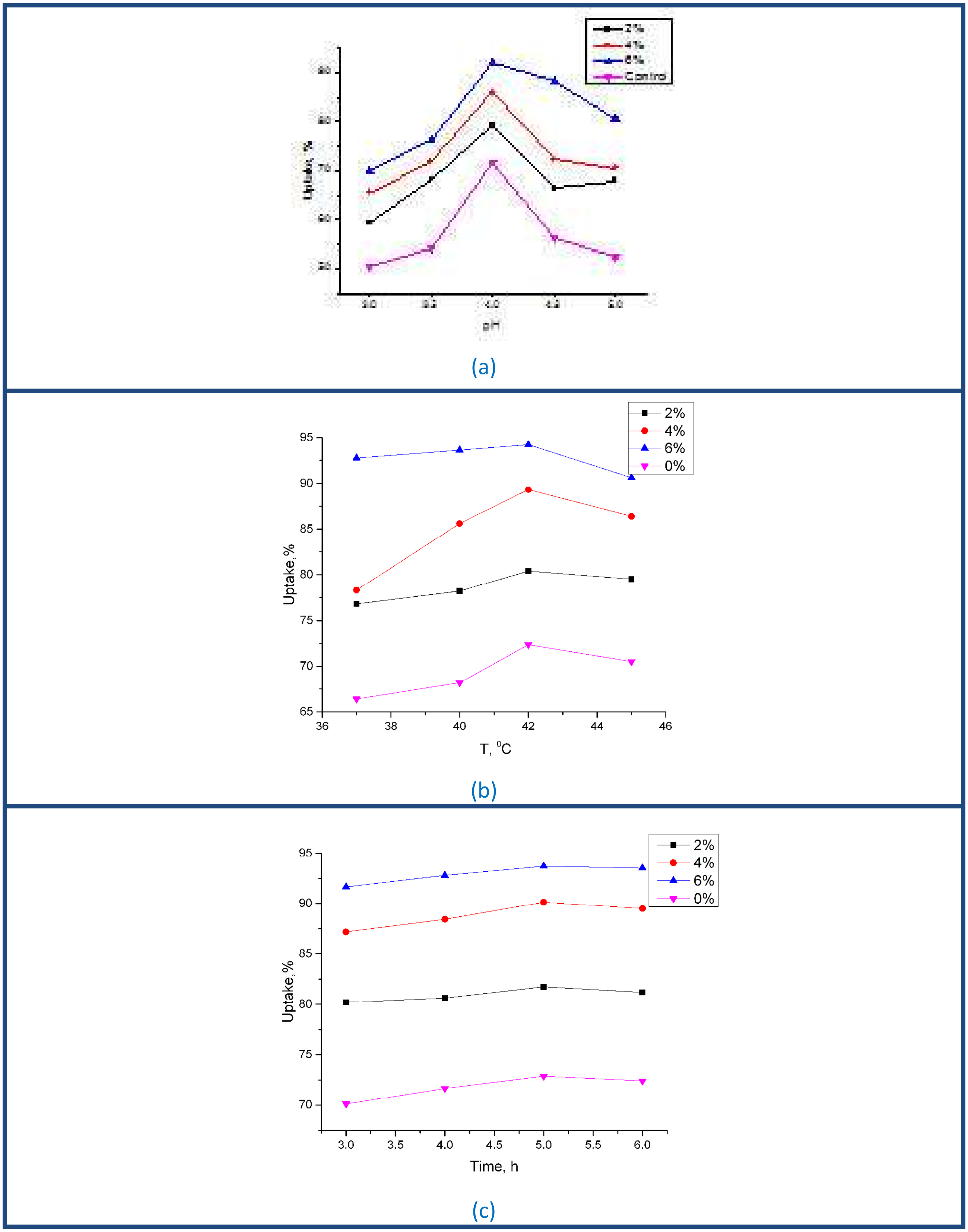
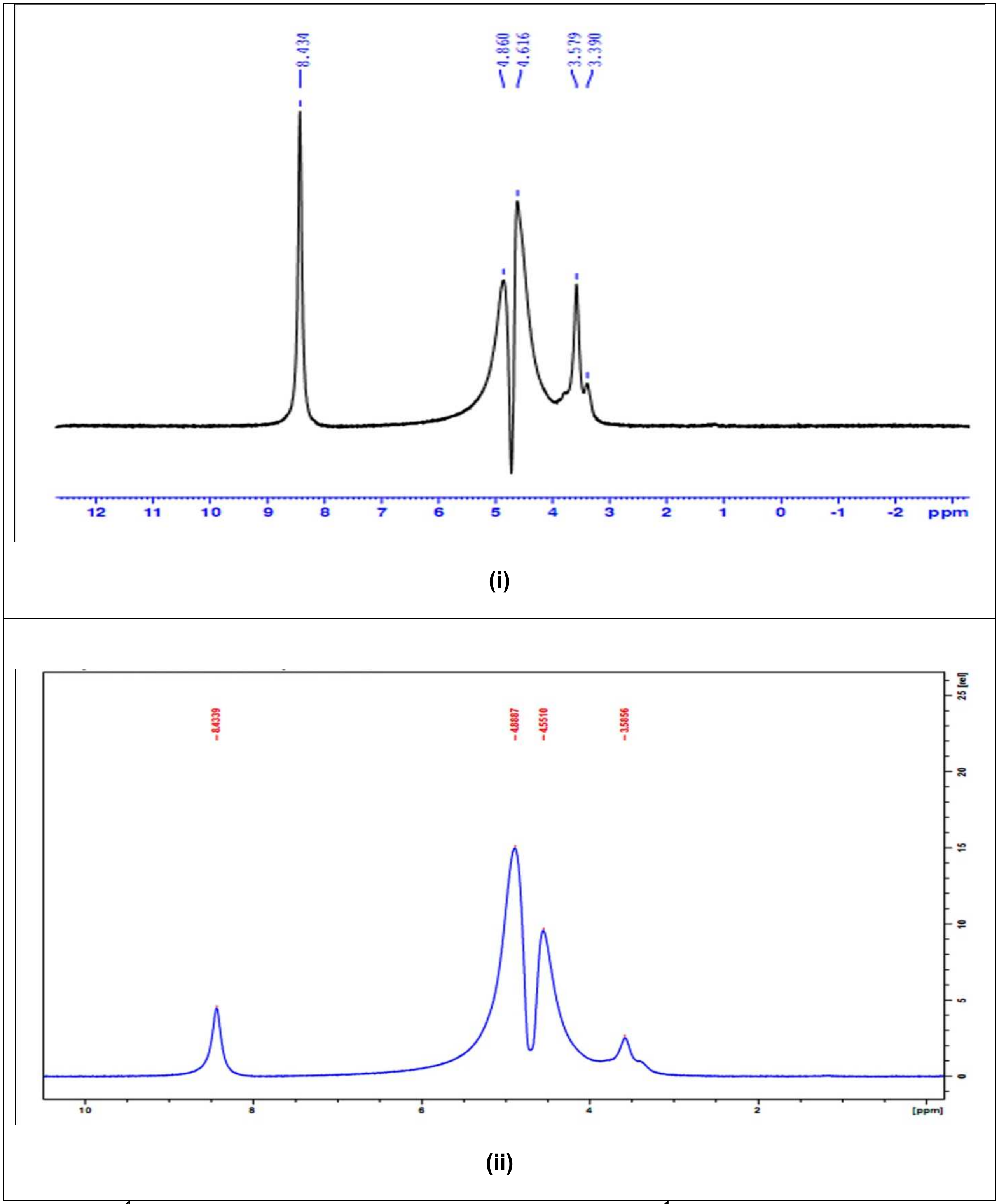


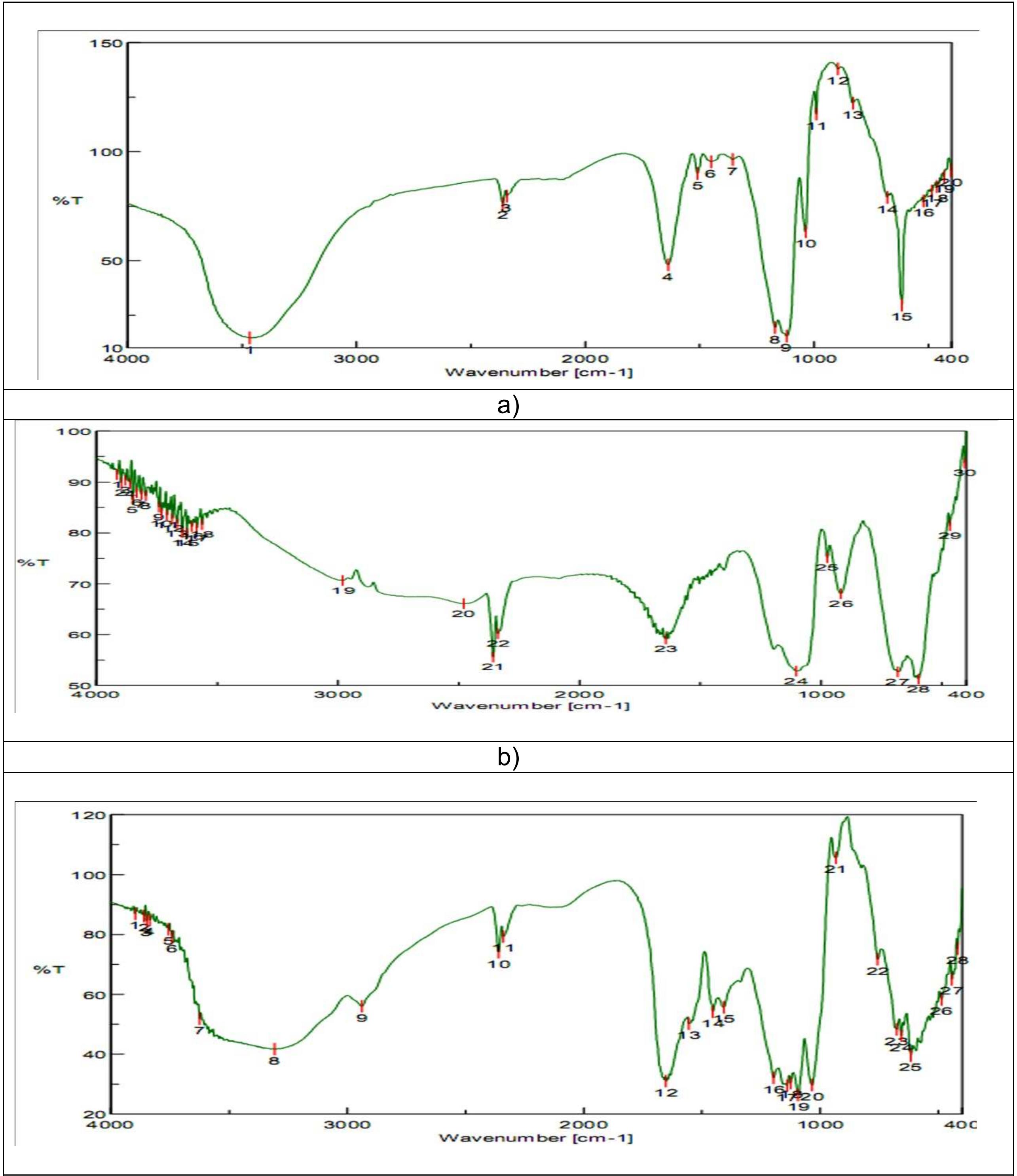
Fig. 2 (a) Variation in Cr (III) absorption with pH (b) variation of Cr (III) absorption with temperature and (c) variation in Cr (III) absorption with duration (time)



(i)

(ii)

Fig. 3 (i) ^{1}H NMR spectra a) pure copolymer sample: (**ii)** ^{1}H NMR spectra b) 2% copolymer treated sample.

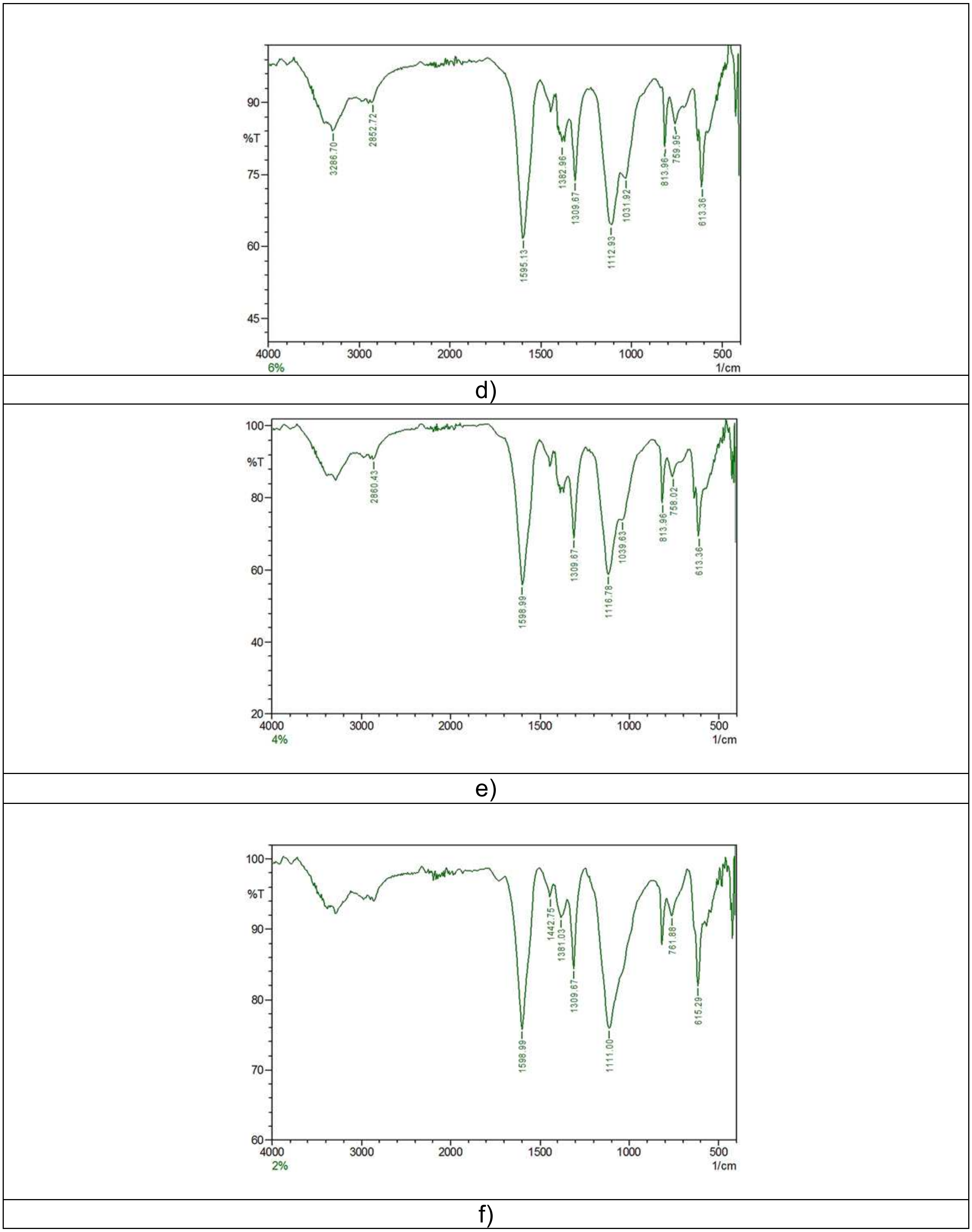


a)

b)

c)

Figs. 4 (a-c) FT-IR spectra for the a) CH sample, b) PVA sample, c) copolymer sample



d)

e)

f)

Figs. 4 (d-f) FT-IR spectra for the d) 6% copolymer treated sample, e) 4% copolymer treated sample, f) 2% copolymer treated sample

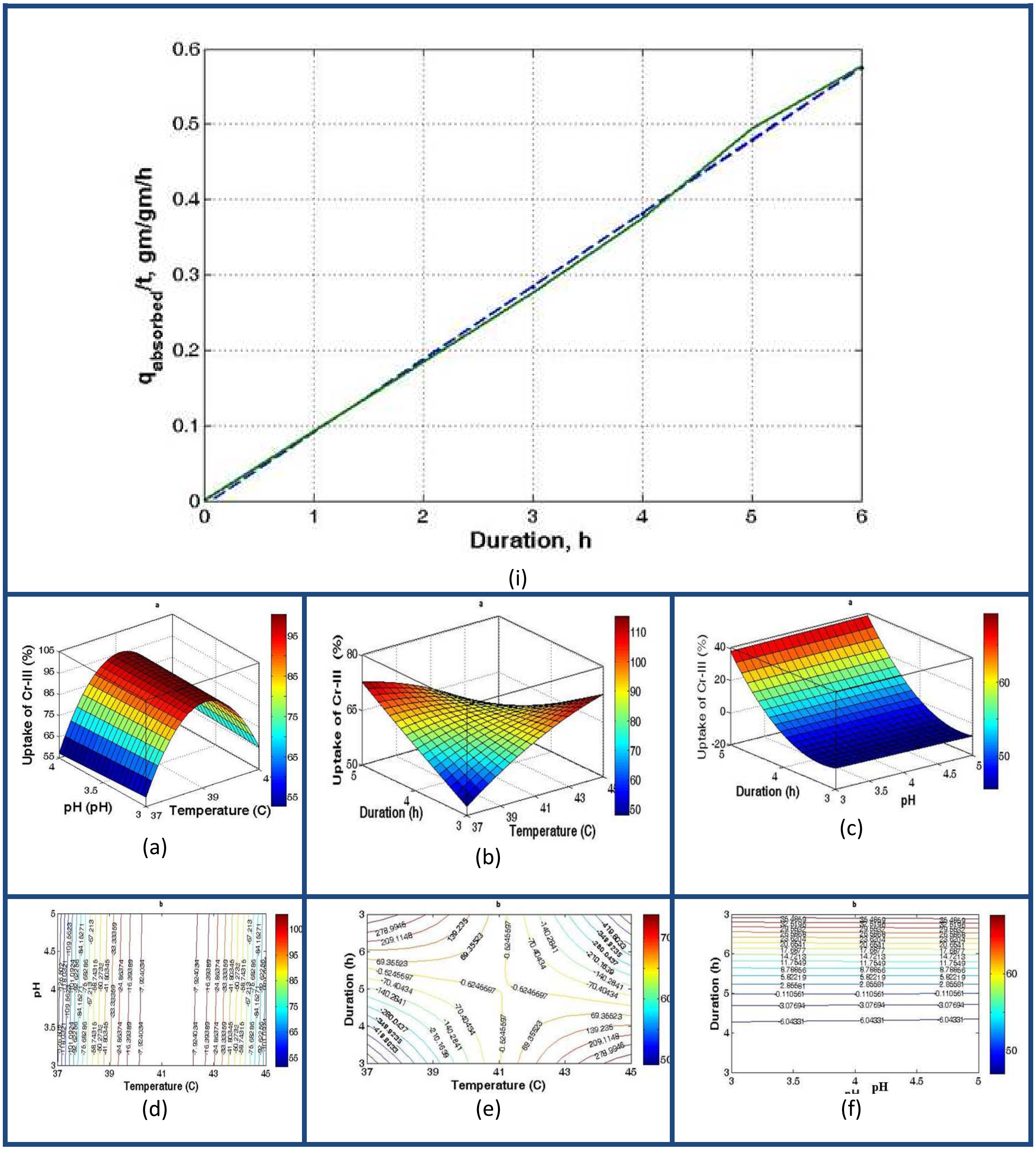


Fig. 5 Kinetics of adsorption of Cr (III) using (i) Langmuir isotherm and Optimization of operating parameters using response surface methodology (a) pH (b) temperature (c) duration and Contour plots of (d) pH-temperature (e) duration-temperature (f) duration-pH

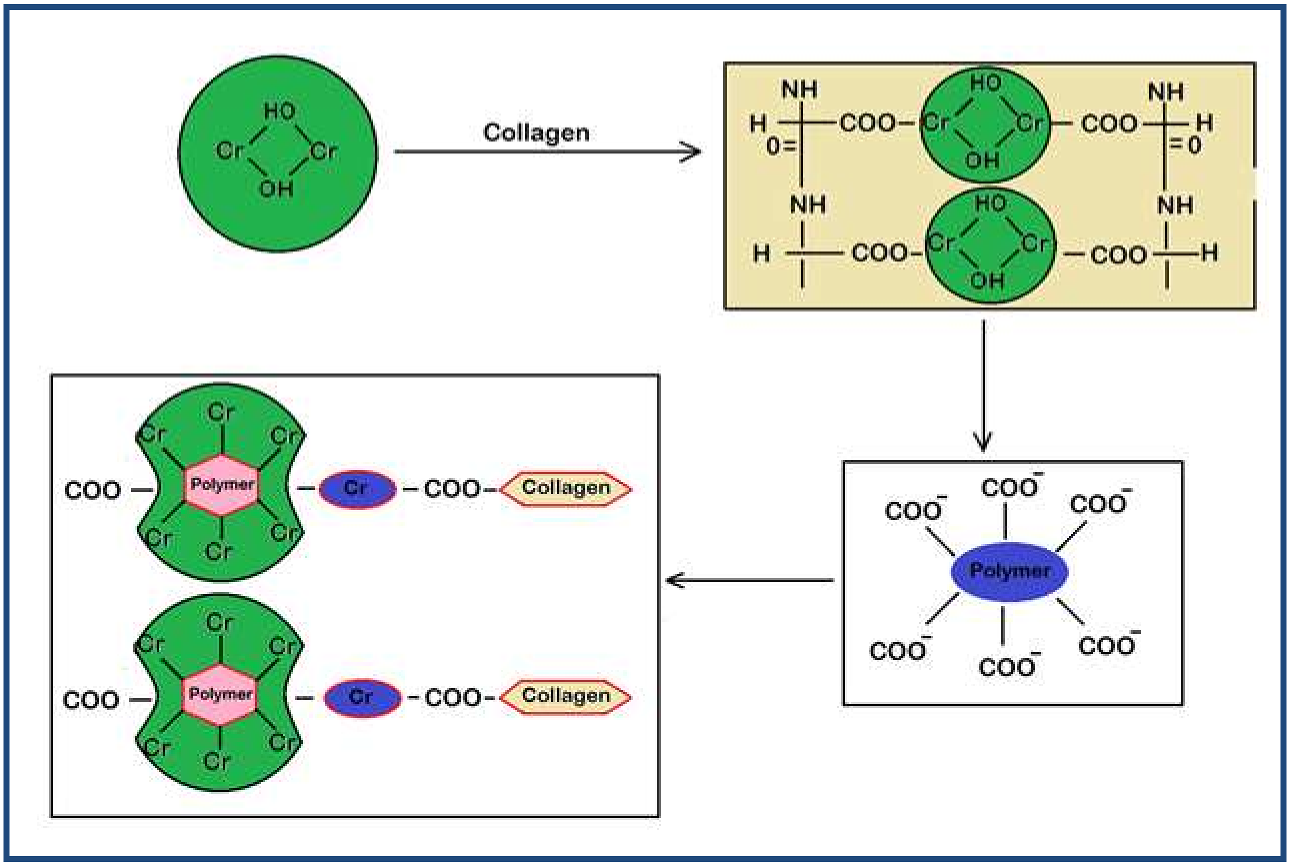
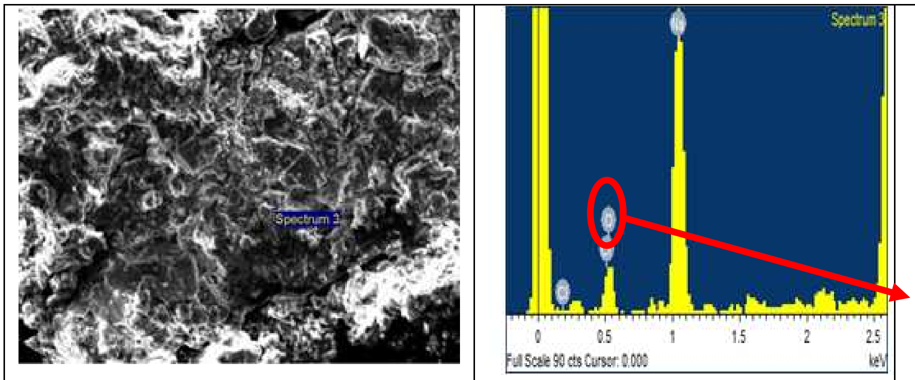
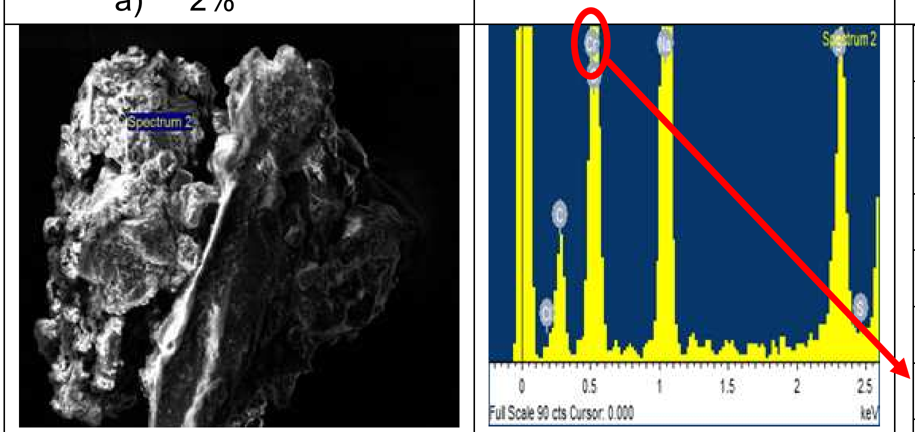


Fig. 6 Plausible mechanism for the adsorption of chromium (III) by co-polymer leading to CPC complex.



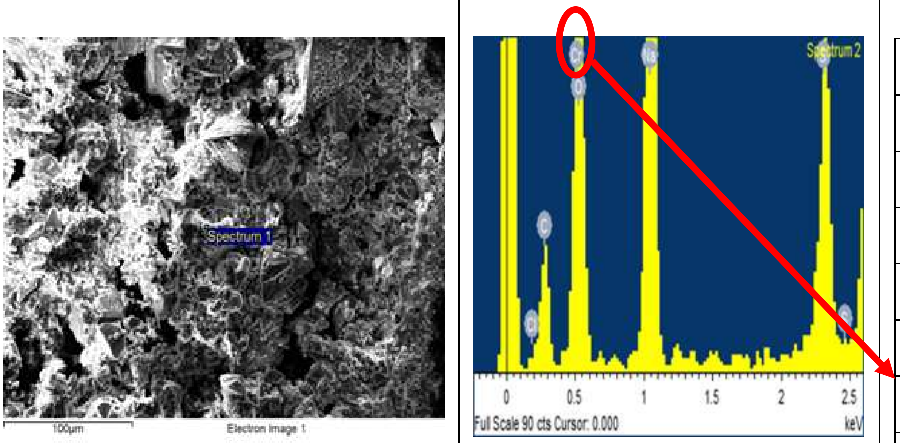
a) 2%

Element	Weight%	Atomic %
O K	17.54	29.69
Na K	20.31	23.93
Cl K	57.66	44.05
Cr K	4.48	2.34
Totals	100.00	



b) 4%

Element	Weight%	Atomic%
C K	29.55	40.74
O K	41.78	43.25
Na K	8.81	6.35
Mg K	5.43	3.70
Cl K	9.19	4.29
Cr K	5.24	1.67
Totals	100.00	



c) 6%

Element	Weight%	Atomic%
C K	23.10	32.56
O K	45.66	48.31
Na K	16.51	12.15
S K	5.82	3.07
Cl K	6.60	3.15
Cr K	2.31	0.75
Totals	100.00	

Fig. 7 SEM-EDX for a) 2% copolymer treated sample, b) 4% copolymer treated sample, c) 6 % copolymer treated sample

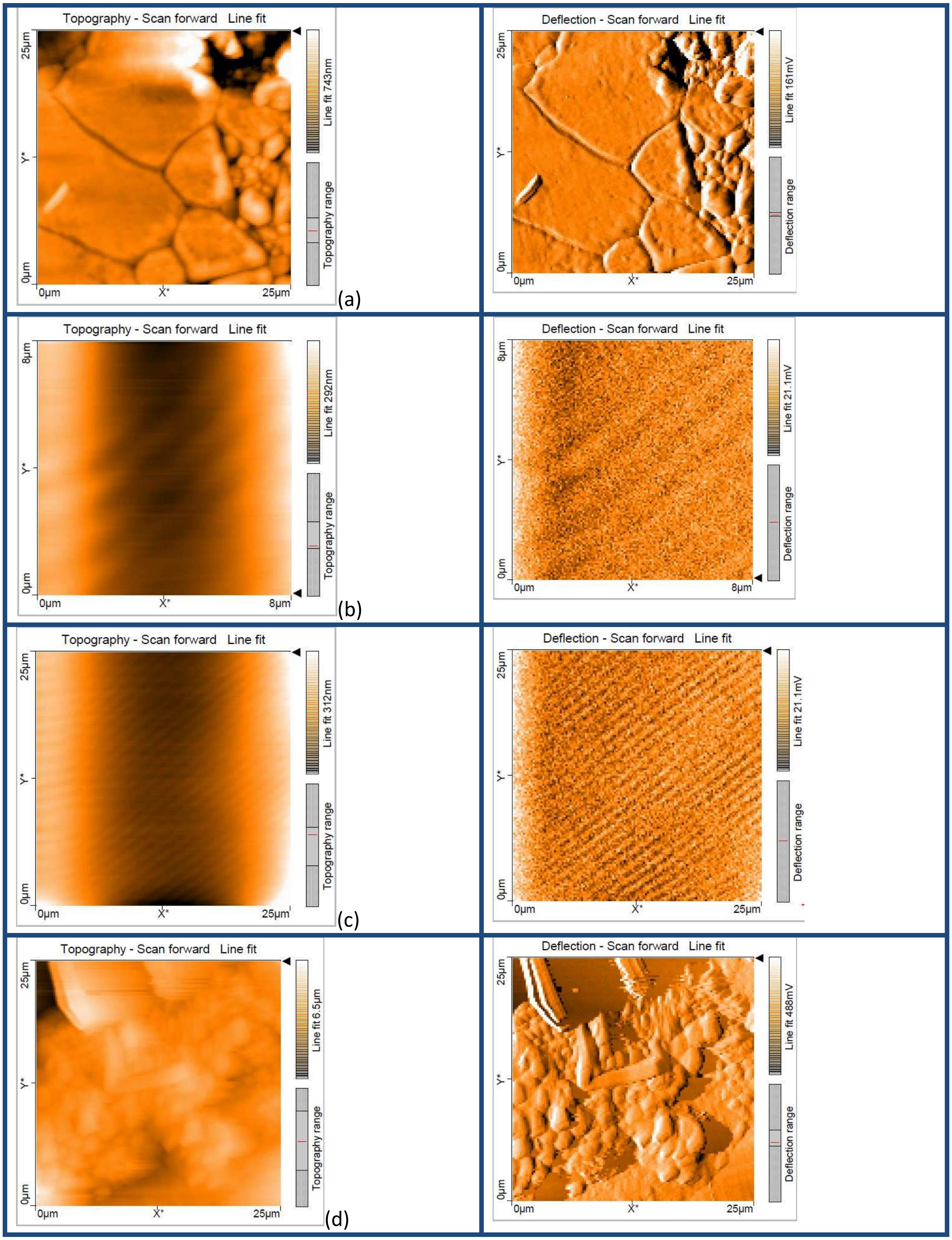


Fig. 8 (t-b) Topography and deflection of prepared (a)copolymer, (b) 2, (c) 4 and (d) 6% copolymer treated sample in the chrome absorption process.

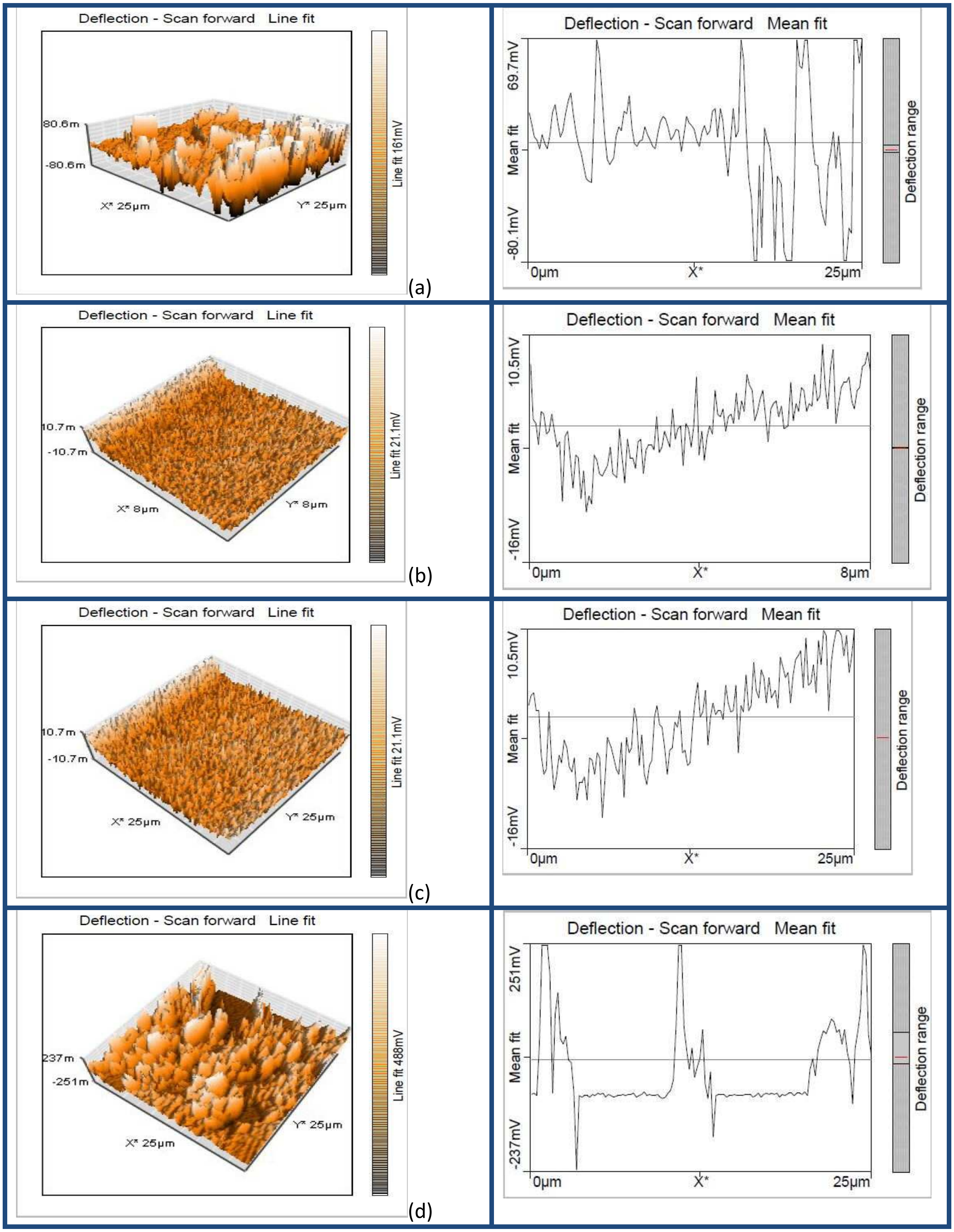
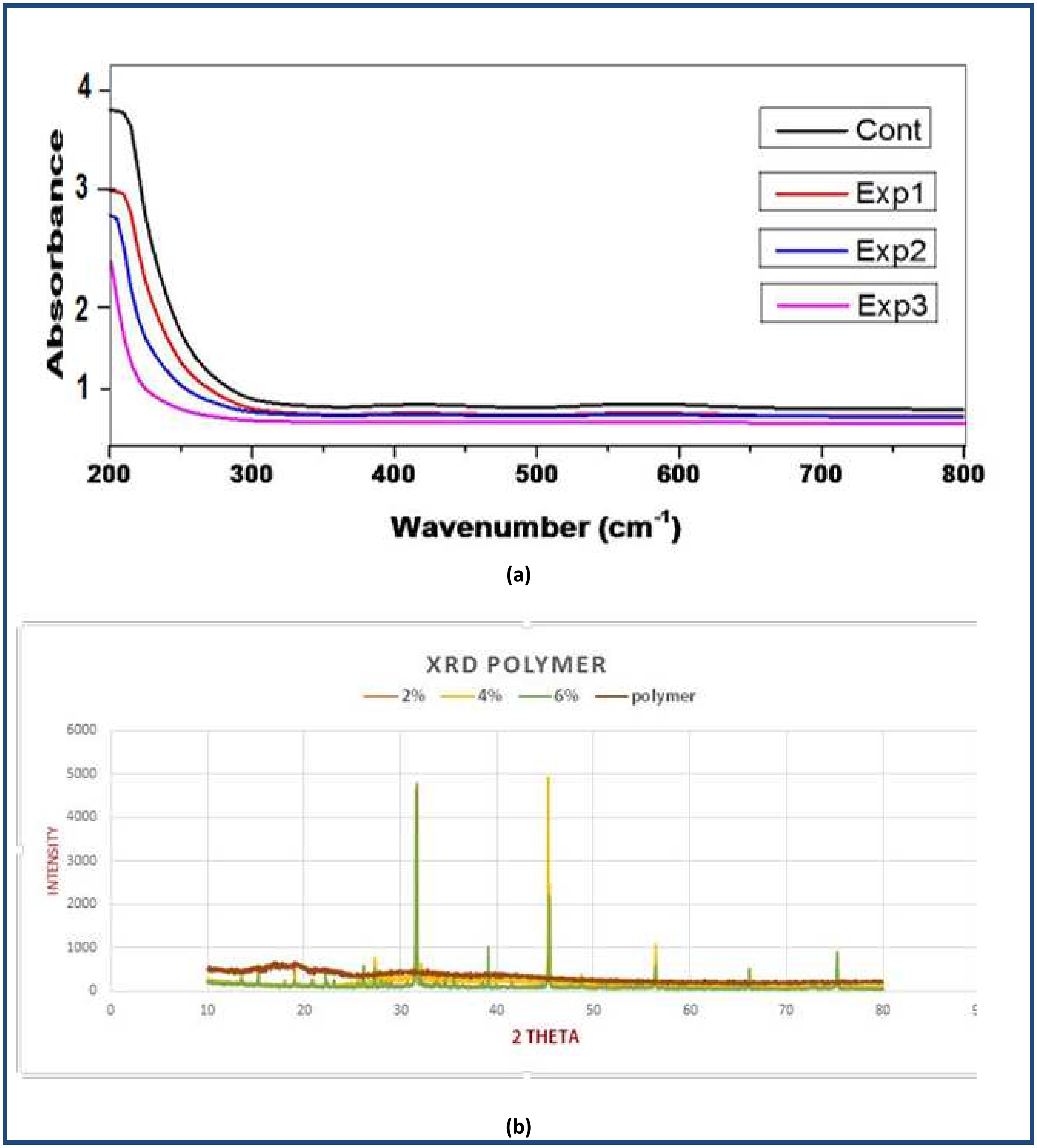


Fig. 9 (t-b) Deflection and mean fit for the pure (a) copolymer, (b) 2, (c) 4 and (d) 6% copolymer treated sample in the chrome absorption process.



(a)

(b)

Fig. 10 UV absorption spectra for Exp-1(2% copolymer treated sample), Exp-2 (4% copolymer treated sample), Exp-3 (6% copolymer treated sample), cont – without treating co-polymer. XRD spectra indicating 2,4 and 6% copolymer treated sample and pure co-polymer sample.

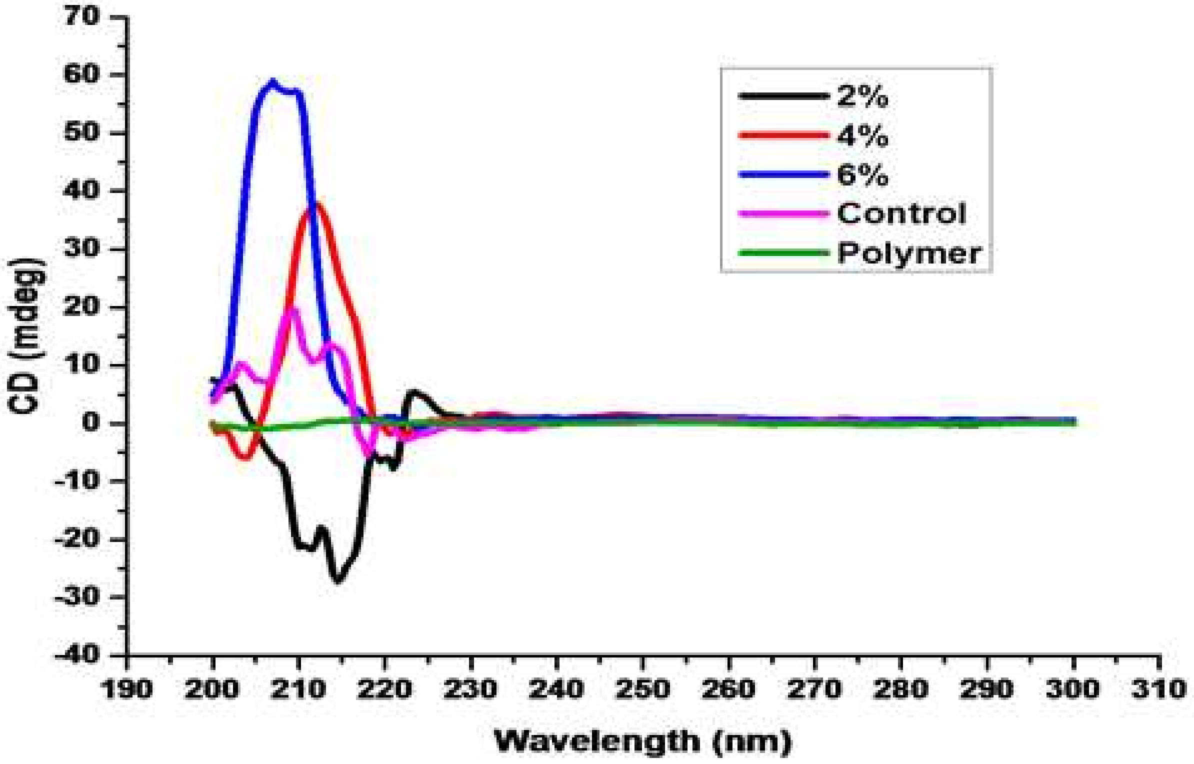


Fig. 11 CD spectra for the 2% copolymer treated sample, 4% copolymer treated sample, 6 % copolymer treated sample, control sample and pure copolymer sample.