



N–C/ O–C Coupled Synthesis Of Scalable Collagen-Polymer Composite Hydrogel For Wastewater Treatment

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Abstract

Multifunctional collagenic proteins (MCPs), one of the most frequently generated hazardous leather wastes, are not properly recycled despite having multiple organic functionalities, such as =N–, =NH, >NH, and –NH₂, because of their particulate appearance. To overcome this problem, MCPs have been internalized herein within the microstructure of starch-grafted-pentapolymer, i.e., starch-g-[itaconic acid (IA)-co-*N*-((3-(isopropylamino)-3-oxopropoxy)methyl)butyramide (NIPAOPMB)-co-*N*-(Hydroxymethyl)acrylamide (NHMA)-co-*N*-(3-((hydroxymethyl)amino)-3-oxopropyl)-*N*-isopropylbutyramide (NHMAONIB)-co-*N*-isopropylacrylamide (NIPA)], to obtain a novel multifunctional hybrid Collagen-Polymer Composite, i.e., **CPC**. Here, the synthesis has been carried out through concerted-step polymerization of MCP, starch, and synthetic monomers, i.e., IA, NHMA, and NIPA, and in situ N–C/ O–C coupled strategic allocation of fourth and fifth comonomers, i.e., NIPAOPMB and NHMAONIB. Structures of **CPC** and metal-ion adsorbed **CPC**; grafting of starch; **MCP**-internalization; and superficial characterization have been analyzed by NMR, FTIR, XPS, and SEM. The as-obtained **CPC** has not only exhibited the extraordinary adsorption capacity towards Pb(II) and AsO₄³⁻ at the working pH of 7 and 4, respectively, but has also provided an avenue for treating waste effluents of industries by using industrial solid wastes. This project will ensure liquid

waste treatment of industries by using solid industrial wastes, hence will contribute significantly towards minimizing investments for reducing environmental pollution.

Introduction

Presently, the use of scalable-and-reusable low-cost hybrid polymer-composites, synthesized from multipolymers and multifunctional solid bio-wastes are receiving much attention for adsorption removals of harmful industrial wastes from leather, paints, agrochemicals, textile, and pharmaceuticals [1,2]. In this context, collagenic solid wastes of leather industries, such as multifunctional collagenic proteins (MCPs), though are multifunctional, yet lack in large scale industrial applications [3]. The most common disposal techniques of MCPs are still limited to incineration and land filling, which are highly detrimental to environment [4]. However, being chemically treated, MCPs contain variegated functionalities including to those of pure collagen. Despite variable functionalities, $-NH_2$, $>NH$, $=NH$, and $=N-$, MCPs are very tough to be utilized as adsorbents because of the tiny particulate appearance. Therefore, suitable physical and support are essential to utilize particulate MCPs as adsorbents. Since MCPs are rich in nitrogen-containing functionalities, suitable for adsorbing anions at low pH, MCPs have been utilized herein to adsorb AsO_4^{3-} . Starch-g-[itaconic acid (IA)-co-*N*-((3-(isopropylamino)-3-oxopropoxy)methyl)butyramide (NIPAOPMB)-co-*N*-(Hydroxymethyl)acrylamide (NHMA)-co-*N*-(3-((hydroxymethyl)amino)-3-oxopropyl)-*N*-isopropylbutyramide (NHMAONIB)-co-*N*-isopropylacrylamide (NIPA)], i.e., starch-g-pentapolymer, has been utilized herein as the support of MCPs. Therefore, MCP-internalized-starch-g-pentapolymer hydrogel, i.e., Collagen-Polymer Composite/ **CPC**, has been synthesized herein. The **CPC** possess the excellent balance within *O*- and *N*-donors, suitable for adsorbing both cations/ anions. Importantly, though few attempts reported pentapolymer synthesis from five ex situ monomers [5–7], the strategic design-and-synthesis of a hybrid polymer composite, comprising natural (i.e., starch), synthetic (pentapolymer), and semisynthetic (MCP) macromolecules and in situ protruded two new multifunctional comonomers is yet to be reported.

Naturally occurring arsenic primarily cumulates through anthropogenic actions and natural weathering processes including coal ash disposal, mining, and pesticide treatment. As(V) damages DNA, fats, proteins, and carbohydrates, and brutally deteriorates botanical growth, metabolism, and reproduction [8,9]. In human body, As(V) causes cancer; skin disease; hypertension; dysfunction in bladder, kidney, and lungs; pneumonia; and coronary heart diseases [10,11]. Again, Pb(II) induces health problems including infertility, neural dysfunction, muscle/ joints pain, irritability, and loss of memory [12]. Therefore, removals of As(V) and Pb(II) via cheap and sustainable technologies are

attracting much attention to protect eco-system, atmosphere, and living bodies. Of different methods including reduction, reverse osmosis, ion exchange, solvent extraction, coagulation, membrane-aided separation, chemical precipitation, and adsorption, adsorption is mostly adopted because of simple instrumentation, easy handling, cheap, versatility, accuracy, and reusability of the same adsorbent. Though few adsorbents, such as activated sludge [13], biochar [14], metal-biochar composite [11], nanocomposite [15], and fluorescent polymers [16], have been utilized for adsorbing As(V)/ Pb(II), hybrid polymer composites are still unexplored for adsorbing As(V)/ Pb(II).

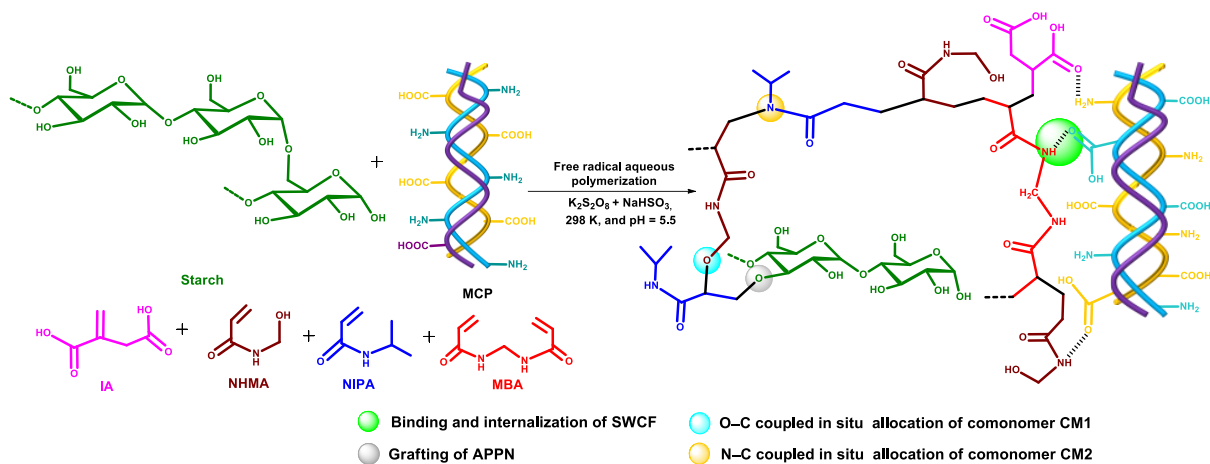
Experimental section

Materials

IA, NHMA, NIPA, Starch, MCP, MBA, $K_2S_2O_8$, $NaHSO_3$, Na_3AsO_4 , and $Pb(NO_3)_2$ were purchased from Merck and used as-received.

Synthesis of CPC

For synthesizing **CPC**, 0.60 g Starch was dissolved in 35 mL conductivity water at 60 °C with constant stirring at 300 RPM. Then, 2.29 g IA was dissolved in 14 mL conductivity water, neutralized by saturated NaOH solution, and transferred to the viscous Starch solution. Then, to this mixture, 11 mL 9.56 [M] NIPA, 11 mL 5.23 [M] NHMA, and 9 mL 0.20 [M] aqueous MBA solutions and 0.20 g dried MCP were added at 25 °C. After homogenization, 10 mL 0.24 [M] $NaHSO_3$ and 10 mL 0.09 [M] $K_2S_2O_8$ aqueous solutions were added to initiate polymerization. The obtained **CPC** was washed with IPA/ H_2O mixture and dried for 5 days.



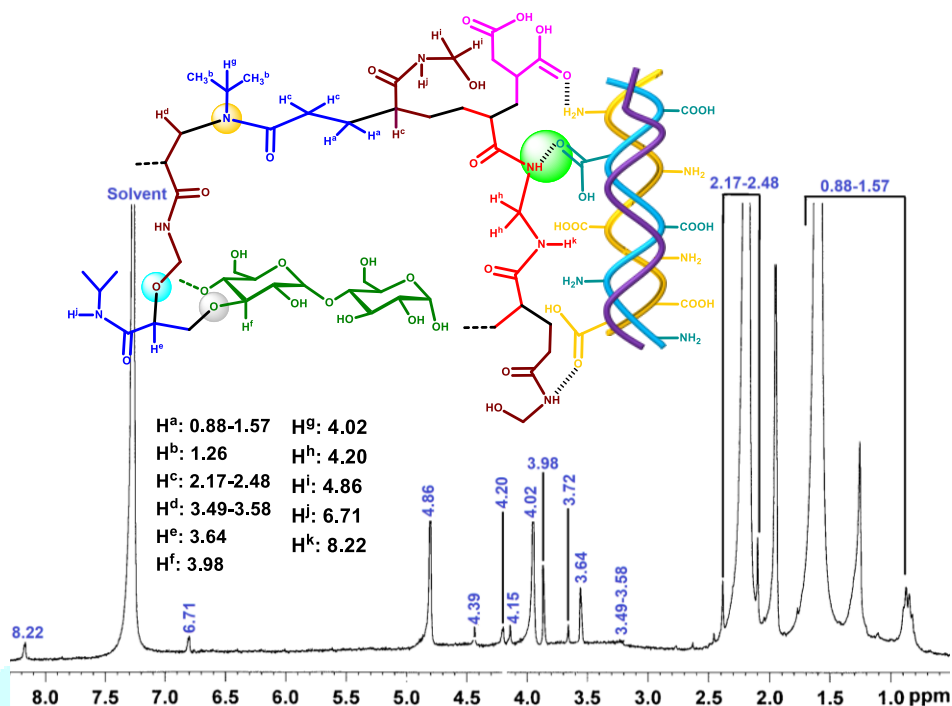
Characterization

Structure of **CPC** and nature of bonding in **Pb(II)-CPC** and **AsO₄³⁻-CPC** were elucidated through NMR, FTIR, XPS, and SEM, and pH_{PZC}.

Results and discussion

Characterization of CPC

In **CPC**, the arrival of $-\text{CH}_2(\alpha)-/ >\text{CH}-$ and $-\text{CH}_2(\beta)-$ moieties were confirmed by ¹H NMR peaks within 2.17–2.48/ 0.88–1.57 ppm (Fig. 1) and $-\underline{\text{C}}\text{H}_2-/ >\underline{\text{C}}\text{H}-$ binding energy (BE) at 284.62 eV (Fig. 2a). The C–C coupled complete polymerization was further substantiated from the loss of vinyl peaks within 5.78–6.32, 5.70–6.37, 5.60–6.22, and 5.59–6.13 ppm of IA, NHMA, NIPA, and MBA, respectively, and simultaneous obsolescence of C–H *def.* and *overtone* of $\text{CH}_2=\text{CRR}'$ (R= $-\text{COOH}/\text{H}/\text{H}/\text{H}$ and R' = $-\text{CH}_2\text{COO}-/ -\text{CONHCH}_2\text{OH}/ -\text{CONHCH}(\text{CH}_3)_2/ -\text{CONHCH}_2-$ for IA/ NHMA/ NIPA/ MBA) at 910 and 1830 cm^{-1} , respectively (Fig. 2g). Again, incorporation of NHMA, NIPA, and MBA in **CPC** was confirmed by $-\text{CH}_2-$ peaks of NHMA/ MBA and $>\text{CH}-/ -\text{CH}_3$ peaks of NIPA at 4.86/ 4.20 and 4.02/ 1.26 ppm, respectively. Amide I/ III peaks of $-\text{CONH}-$ at 1634/ 1268 cm^{-1} justifying presence of NHMA, NIPA, and MBA in **CPC**, respectively. Moreover, N–H of NHMA/ NIPA and MBA appeared at 6.71 and 8.22 ppm, respectively. Significantly, in situ protruded new comonomer, i.e., NHMAONIB, in **CPC**



through O–C coupled $-\text{CONHCH}_2\text{OCH}_2\text{CH}(\text{CONH}-)$ linkage was confirmed by peaks at 3.64 ppm, supported by $-\text{CH}_2-$ *def.* of $-\text{CH}_2-\text{O}-\text{CH}_2-$ at 1128 cm^{-1} , and C1s/ O1s BEs of $-\text{CONHCH}_2\text{OCH}_2\text{CH}(\text{CONH}-)$ at 286.11/ 531.51 eV (Fig. 2b). Again, N–C coupled in situ protruded fifth comonomer-derivative via $-\text{CON}(\text{CH}(\text{CH}_3)_2)\text{CH}_2\text{CH}(\text{CONH}-)$ linkage was inferred through fresh peaks within 3.49–3.58 ppm in **CPC**, substantiated from N–C=O *def.* peak of $-\text{CON}<$ at 586 cm^{-1} . In fact, N–C coupling was further inferred by O1s shake-up satellite peak of $-\text{CON}<$ at 539.31 eV. In **CPC**, the grafting of starch was confirmed from the shifting of starch specific $>\text{CHOH}$ peak of H^b and $-\text{CH}_2\text{OH}$ peak of H^c from 3.93 and 3.85 ppm of starch to 3.98 and 3.72 ppm in **CPC**, respectively, suggested by $-\text{CH}_2-$ *asym. str./ sym. str.* of $>\text{CH}-\text{O}-\text{CH}_2-$ / $-\text{CH}_2-$ *def.* of $-\text{CH}_2-\text{O}-\text{CH}_2-$ at $2964/ 2873/ 1056\text{ cm}^{-1}$. In **CPC**, the presence of MCP was understood via amino acid peaks, such as $\alpha\text{-H}$ of Gly and $\alpha\text{-H}/ -\text{CH}_3$ of Ala at 4.15 and 4.39/ 1.35 ppm, respectively.

Characterization of AsO_4^{3-} -CPC and Pb(II) -CPC

In AsO_4^{3-} -**CPC**, the ionic bonding within AsO_4^{3-} and $-\text{NH}_3^+$ of **CPC** (at $\text{pH} < \text{pH}_{\text{PZC}}$) was inferred by the increase in N1s BE from 401.05 eV in **CPC** to 400.69 eV in AsO_4^{3-} -**CPC**

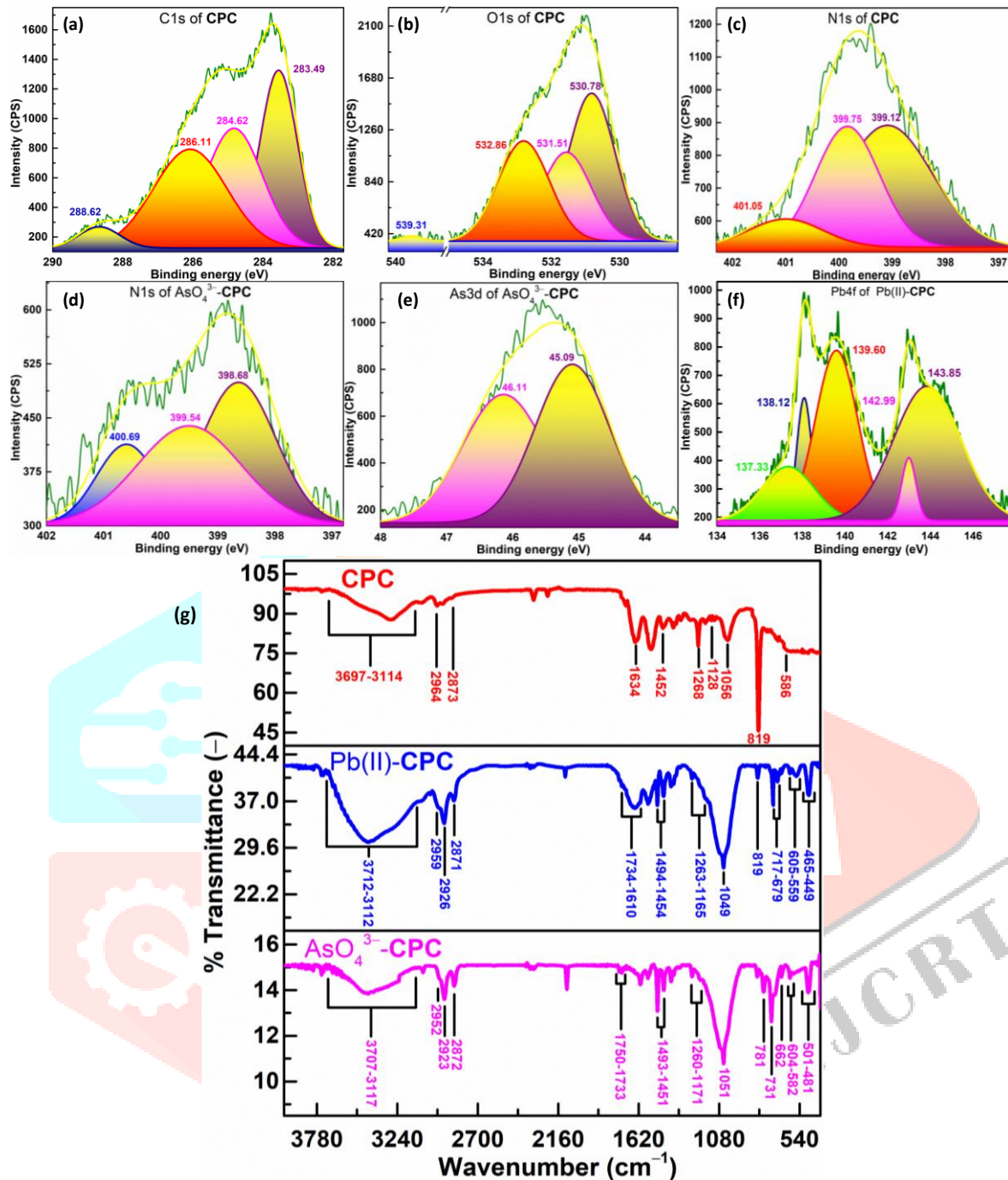


Fig. 2. (a-f) XPS and (g) FTIR of **CPC/ Pb(II)-CPC/ AsO₄³⁻-CPC**

(Fig. 2c,d), respectively, supported by the reduction in As3d_{5/2}/ 3/2 BEs from 45.65/ 46.80 eV in As(V)-salts to 45.09/ 46.11 eV in AsO₄³⁻-CPC (Fig. 2e). The coordination in AsO₄³⁻-CPC was further supported by the superficial crystalline flaky depositions from SEM photomicrographs (Fig. 3). In Pb(II)-CPC, the prevalence of ionic and coordinate bonding

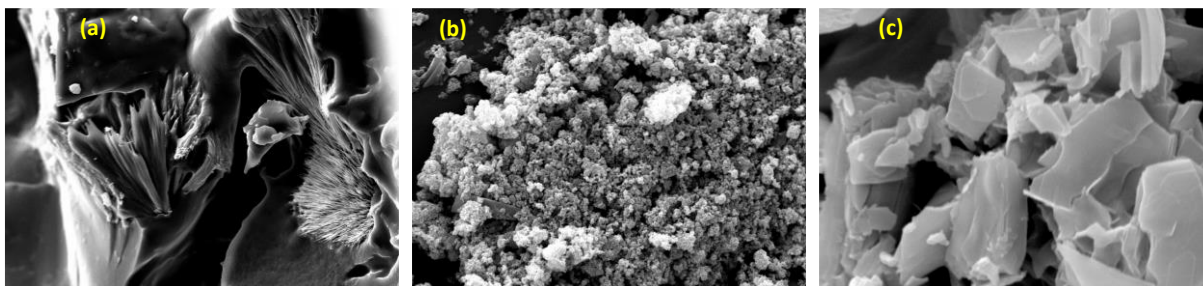


Fig. 3. SEM photomicrographs of (a) **CPC**, (b) **Pb(II)-CPC**, and (c) **AsO₄³⁻-CPC**

within Pb(II) and COO^- (at $\text{pH} > \text{pH}_{\text{PZC}}$) was inferred from the change of $\text{Pb}4f_{7/2}$ and $\text{Pb}4f_{5/2}$ BEs from 139.30 and 143.80 eV of pure Pb(II) to 137.33/ 138.12/ 139.60 and 142.99/ 143.85 eV (Fig. 2f), respectively, in Pb(II)-**CPC**. Moreover, peaks at 137.33/ 138.12 eV substantiated superficial deposition of lead acetate/ basic lead acetates on Pb(II)-**CPC**, supported by the Pb–O peak at 465/ 449 cm^{-1} .

Adsorption of AsO_4^{3-} and Pb(II) by CPC

Despite trying with several isotherms including Langmuir, Sips, Henry, Freundlich, and BET, equilibrium adsorption data fitted best with Langmuir isotherm, justified from the highest adjusted R^2/F and lowest χ^2 values. The q_{max} was in the order of AsO_4^{3-} (178.49 mg g^{-1}) > Pb(II) (170.35 mg g^{-1}) because of the charge densities on pollutants.

Conclusions

Herein, scalable multifunctional hybrid hydrogel, i.e., **CPC**, has been synthesized via internalization of hazardous particulate MCPs within pentapolymer moiety synthesized by polymerizing IA, NHMA, and NIPA monomers; grafting of Starch; and strategic in situ protrusion of two new comonomers. The as-synthesized CPC exhibited excellent adsorption capacity towards anionic AsO_4^{3-} and Pb(II). This eco-friendly multifunctional adsorbent prepared via entrapping hazardous waste collagenic particles is expected to accomplish the rebellion demand of inexpensive, swift, and selective waste treatment of MSMEs.

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