Bifunctional Hybrid Composites from Collagen Biowastes for Heterogeneous Applications

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ABSTRACT: We report the synthesis of an electrically conductive and magnetically active hybrid biocomposite comprising collagen and polyaniline (PAni) as the matrix and iron oxide nanoparticles (IONPs) as the filler through an in situ polymerization technique. Here, the matrix biopolymer, collagen, was extracted from trimmed wastes of animal hides generated from the leather industry. The as-synthesized C/PAni/IONP hybrid biocomposite powder possesses excellent electrical conductivity, thermal stability, and saturation magnetization, thereby providing scope for a wide range of applications. We show that the bifunctional composite has an ability to conduct electrons using a light emitting diode and battery setup, degrade dye under sunlight owing to its inherent photocatalytic activity, and absorb oil from oil–water mixtures with easier collection under magnetic tracking. We also demonstrate that the composite has remarkable electromagnetic interference shielding in the X-band frequency range. The results suggest that biowastes can be converted into useful high-value hybrid materials for applications in catalysis, biological, electronic, and environmental fields, thereby presenting a scalable and sustainable approach.

1. INTRODUCTION

Functional materials with diverse properties are in great demand for a wide range of applications.1–3 Composites are ideally suitable to attain the desirable multifunctionality by the precise assembly of specific materials to get the broad spectrum of desired properties such as electrical conductivity, magnetism, thermal stability, mechanical stability, biodegradability, and biostability. Approaches have been made to develop composites with complex nanoscale features for catalysis,4,5 water treatment,6,7 heavy-metal removal,8 oil spill remediation,9 and electromagnetic interference (EMI) shielding applications.10,11 Polyaniline (PAni) is the most widely used intrinsically conducting polymer in several applications because of its relatively facile processability, mechanical flexibility, low cost, excellent electrical conductivity, and environmental stability.12,13 Several studies have been carried out using PAni for sensors, light emitting diodes (LEDs), photocatalysis, EMI shielding, electrostatic discharge (ESD) protection, capacitors, and battery applications.14–19 PAni-decorated cellulose aerogel nanocomposites showed a better methylene blue dye degradation through the photocatalytic activity.4 In situ polymerized PAni/multiwalled carbon nanotube (MWCNT) composites exhibited an absorption-dominant total shielding effectiveness (SE) of 39.2 dB in the Ku-band frequency.10 PAni-functionalized MWCNT/polystyrene composites displayed a total SE of −23.3 dB.11 Iron oxide nanoparticles (IONPs) are immensely applied in the field of terabit magnetic storage devices, catalysis, sensors, color imaging, electromagnetic shielding, and high-sensitivity biomolecular magnetic resonance imaging for medical diagnosis and therapeutics.20–24 However, these applications require a coating of IONPs through the polymeric compounds to improve the stability and dispensability of the particles.21,25 The blending of IONPs with the conducting polymer matrix enhanced their stability and applicability in the photocatalysis, oil absorption and removal, and electromagnetic shielding.26,27 The incorporation of IONP/polypyrrole with an epoxy resin matrix showed an enhanced EMI absorption shielding effectiveness of 10.1 dB at 17–18 GHz.28

Collagen (C) is an abundant fibrous protein with weak antigenicity and excellent biocompatibility and biodegradability properties.29,30 It has been widely used in tissue engineering and biomedical applications.30 Its high biodegradability property compared to other synthetic polymeric matrices such as poly(2,5-dimethoxyaniline), polyimide, and epoxies could be exploited as a potential biopolymeric matrix for various environmentally sustainable applications. On the other hand, enormous quantities of collagenous solid wastes are generated from leather industries.31 The utilization of collagen from the wastes reduces the environmental impact and also...

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provides economic returns. For instance, we have shown a promising oil absorption and removal application using iron oxide-stabilized collagen matrices based on the concept of utilizing an industrial waste to remove another waste.\textsuperscript{6,32} Recently, we also reported the synthesis of collagen/polypyrrole hybrid aerogel with enhanced biostability and good electrical conductivity.\textsuperscript{33} However, the electrical conductivity attained by the hybrid aerogel is not sufficient for the effective shielding of the electromagnetic radiation. Here, we synthesized a hybrid biocomposite powder with high electrical conductivity and magnetic properties using the compositions of collagen, PAni, and IONPs through an in situ chemical oxidative polymerization technique. The induced high electrical and magnetic properties enrich the composite functionality to possess a synergistic EMI shielding protection and magnetic treatment capabilities. The composite powder may act as a hybrid conductive filler in insulating matrices or a coating over the insulating components of electronic appliances for EMI shielding and ESD protection. The as-synthesized C/PAni/IONP hybrid biocomposites were investigated for structural, electrical, thermal, magnetic, photocatalytic, oil absorption and removal, and EMI shielding studies.

2. RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) spectra of pure collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite are shown in Figure 1a–d. The FTIR spectrum of the pure collagen depicts the characteristic peaks at 3318, 1653, 1545, and 1290 cm\textsuperscript{−1} corresponding to hydroxyl, amide I, amide II, and amide III groups, respectively (Figure 1a),\textsuperscript{33} whereas the pure PAni exhibits the characteristic bands at around 1583 and 1493 cm\textsuperscript{−1} corresponding to the C–C stretching of quinoid and benzenoid rings, respectively, which indicates the conducting state of doped PAni structures (Figure 1b).\textsuperscript{34} The FTIR spectrum of IONPs depicts the characteristic peak at 582 cm\textsuperscript{−1} corresponding to the Fe–O vibration, whereas the bands at 1128, 1392, and 1623 cm\textsuperscript{−1} are due to the C–O stretching, symmetric stretching, and asymmetric stretching of COO\textsuperscript{−} of citrate, respectively (Figure 1c).\textsuperscript{21}

FTIR spectrum of the C/PAni/IONP hybrid biocomposite exhibits the major peaks at 1582, 1494, 1230, 1149, 1031, 709, and 570 cm\textsuperscript{−1} (Figure 1d). The bands at 1582, 1494, 1230, 1149, 1031, and 709 cm\textsuperscript{−1} correspond to the characteristic peaks of the C–C stretching of quinoid and benzenoid rings, C–N stretching, C–H in-plane bending, SO\textsuperscript{2−} stretching vibrations, and out-of-plane C–H bending vibrations of the PAni polymer, respectively, whereas the peaks at 1230 and 570 cm\textsuperscript{−1} correspond to the amide III group of collagen and the Fe–O vibration of IONPs, respectively. It is interesting to note that the other characteristic peaks of collagen and IONPs are not visible in the hybrid biocomposite spectrum (Figure 1d). This may be due to the coating of PAni over the collagen and IONP molecules, equivalent to a core–shell type of structure. Hence, the polymerization of PAni dominates the surface characteristics of the core molecules, collagen and IONPs, in the composite matrix. This is further evidenced in the results of the FTIR spectra.

The X-ray diffraction (XRD) patterns of pure collagen, PAni, IONP, and C/PAni/IONP hybrid composite are shown in Figure 1e–h. As can be seen, the pure collagen exhibits a broad diffraction peak at 21°, which may be due to the amorphous nature of pristine collagen molecules (Figure 1e).\textsuperscript{35} The characteristic diffraction peaks of PAni seen at 15, 20, and 25° correspond to the (011), (020), and (200) planes of the emeraldine salt form of the orthorhombic crystalline PAni polymer (Figure 1f).\textsuperscript{35} The IONP pattern shows sharp and intense diffraction peaks at 30, 35, 43, 57, and 62° corresponding to the (220), (311), (400), (511), and (440) reflections, which match well with those of cubic Fe\textsubscript{3}O\textsubscript{4} (magnette, JCPDS no. 85-1436) (Figure 1g).\textsuperscript{36} On the other hand, the C/PAni/IONP hybrid biocomposite exhibits the major characteristic peaks of PAni and IONP molecules (Figure 1h).\textsuperscript{34}
The intense peaks at the 2θ values of 12, 19, and 25° correspond to the (011), (020), and (200) planes of PANi, whereas the peaks at 30, 35, 42, 56, and 62° correspond to the (220), (311), (400), (511), and (440) reflections of Fe3O4 (Figure 1h). It is also interesting to note a small hump in the 2θ regions between 20 and 25°, which may be due to the amorphous collagen molecules in the composite matrix (Figure 1h). These XRD results also confirm the presence of collagen, PANi, and IONPs in the C/PAni/IONP hybrid biocomposite.

Thermogravimetric analysis (TGA) patterns of pure collagen, PANi, IONP, and C/PAni/IONP hybrid biocomposite are shown in Figure 2. As can be seen, the TGA curves of collagen, PANi, IONP, and C/PAni/IONP hybrid composite show a multistage decomposition. The first stage is due to the evaporation of water molecules in the samples. The pure
collagen and the functionalized IONPs exhibit only the second stage of decomposition with the inflection points at 331 and 325 °C, respectively (Figure 2a,c), primarily because of the destruction of the macromolecular structure of collagen and the coating layers of the functionalized IONPs. The doped PAni, on the other hand, exhibited the second, third, and fourth stages of decomposition with the inflection points at 285, 419, and 616 °C, respectively (Figure 2b). The weight loss at 285 °C is due to the loss of bound water (secondary dopant) and the decomposition of primary dopants and low-molecular-weight polymeric chains (oligomers), whereas the weight losses at 419 and 616 °C are associated with the complete decomposition of the polymeric chain. It is interesting to notice that the C/PAni/IONP hybrid biocomposite shows second, third, fourth, and fifth stages of decomposition with the inflection points at 272, 319, 484, and 667 °C, respectively (Figure 2d) because of the presence of moisture, collagen, PAni, and the citrate-coated IONPs in the hybrid biocomposite. The fourth and fifth stages of decomposition in the hybrid biocomposite have substantially enhanced inflection points compared to its constituent materials. The residual (37.1%) in the hybrid composite (Figure 2d) is assigned to the magnetic nanoparticles, which are characterized by their high thermal stability. Hence, the results demonstrate that the existence of PAni and the IONP improved the thermal stability in the as-prepared C/PAni/IONP hybrid biocomposite.

Figure 3a–d shows the scanning electron microscopy (SEM) and digital images of pure collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite. As can be observed, the pristine collagen exhibits a fairly smooth surface, whereas PAni exhibits a tubular morphology with an average particle width of 5 ± 2 μm (Figure 3a,b). The tubular morphology of PAni may be due to the large size of the dopant and the anthraquinone ring in the polymeric structure. The citrate-coated IONPs displayed a spherical morphology with an average particle size of 26 ± 6 nm (Figure 3c), whereas the as-synthesized C/PAni/IONP...
The hybrid biocomposite exhibits a sheathlike structure, predominantly because of the morphologies of PANi and collagen (Figure 3d). The spherical IONPs are distributed uniformly on the surface of the C/PANI/IONP composite and probably coated by the collagen/PANI polymers, as can be seen in the higher magnification SEM image (Figure S1). The particle size distribution of the as-synthesized PANi, IONP, and C/PANI/IONP composite is shown in Figure 3e–g. As can be seen, the PANi, IONP, and C/PANI/IONP composites exhibited average particle sizes of 1709 ± 34.5, 43.1 ± 1.08, and 854.6 ± 9.19 nm, respectively (Figure 3e–g). Compared with the average particle size determined from the SEM image, the IONPs exhibited a slightly bigger particle size, which may be due to the agglomeration of the nanoparticles.

Room-temperature magnetization curves of IONP and C/PANI/IONP hybrid biocomposite are shown in Figure 4, and those for pure collagen and PANi are shown in Figure S2. As can be observed, the IONPs show a ferromagnetic-like hysteresis curve with a saturation magnetization value of 26.1 emu/g (Figure 4a). This value is lower compared with that of the bulk iron oxide because of the small particle size of the nanoparticles and the citrate coating.42 The as-synthesized C/PANI/IONP hybrid biocomposite exhibited a saturation magnetization value of 8.32 emu/g (Figure 4b). The low saturation magnetization of the hybrid biocomposite is primarily due to the diamagnetic nature of collagen and PANi polymers (Figure S2a,b), which form a major composition in the composite and also coat the IONPs (Figure S1). Coating of IONPs by the diamagnetic polymers is expected to reduce the saturation magnetization of IONPs. This results in the low saturation magnetization for the C/PANI/IONP hybrid biocomposite. Further, the lower saturation magnetization value of the as-synthesized functionalized IONPs as a result of their small particle size42 also contributes to the low saturation magnetization value of the C/PANI/IONP hybrid biocomposite.

The electrical conductivities of the pure PANi and the as-synthesized C/PANI/IONP hybrid biocomposite are 2.84 × 10⁻² and 2.44 × 10⁻² S/cm, respectively, which are much higher than those of the pure collagen and IONPs (displaying 5.34 × 10⁻¹² and 7.64 × 10⁻⁵ S/cm, respectively). In order to understand the impact of these values, we carried out an experiment employing a LED lamp and battery setup (Figure 5). When the samples were inserted between the batteries, it can be visibly noticed that the pure collagen scaffold did not illuminate the LED light, whereas the IONPs displayed a low extent of brightness. This may be due to the insulating nature of collagen and the semiconducting nature of IONPs (Figure 5a,c). On the other hand, the as-synthesized C/PANI/IONP hybrid biocomposite exhibited a substantially brighter illumination nearly comparable to that of PANi (Figure 5b,d), which has the highest brightness. The extent of brightness is predominantly dependent on the content of PANi in the composite matrix. The enhanced electrical conductivity in the as-synthesized C/PANI/IONP hybrid biocomposite is expected to have potential applications in sensors, bioelectronics, and EMI shielding.

The photocatalytic activity of the constituent materials and the C/PANI/IONP hybrid biocomposite was evaluated by analyzing their efficiency of methylene blue dye degradation under visible-light irradiation monitored through UV–vis (UV–vis) absorbance spectra. The UV–vis absorption spectra and the percentage of methylene blue degradation of the control (without catalyst), collagen, PANi, IONP, and C/PANI/IONP hybrid biocomposite are shown in Figure 6. As can be observed, the methylene blue degradation using the pure
collagen scaffold is only up to 7% at the end of 2 h incubation, which is also similar to that of the control (without catalyst) (Figure 6a,b,f). It clearly shows that the pure collagen scaffold does not have any photocatalytic behavior on the methylene blue degradation, whereas the pure PANi and IONP enhanced the methylene blue degradation up to 49 and 68%, respectively, at the end of 2 h incubation (Figure 6c,d,f). On the other hand, the as-synthesized C/PAni/IONP hybrid biocomposite demonstrates a maximum methylene blue degradation of 81% at the end of 2 h incubation (Figure 6e,f). It is also important to note

Figure 7. Digital photographic images showing the oil absorption and removal of the C/PAni/IONP hybrid biocomposite at different time intervals. (a) Oil and water mixture, (b) sample incubation at 0th second, (c) 10th second, and (d) 30th second. The inset shows the C/PAni/IONP pellet used for the oil absorption and removal studies.

Figure 8. (a) Schematic showing the interaction of electromagnetic wave with the shielding material; EMI SE of the as-synthesized C/PAni/IONP composite at various thicknesses from (b) 1 mm (c) to 1.5 mm to (d) 2 mm measured in the frequency range of 8−12 GHz (X-band).
that the time required for the maximum degradation of the dye is about 20 min beyond which there is no significant degradation occurred. These results suggest that the as-synthesized C/PAni/IONP hybrid biocomposite powder has a great potential in the treatment of dye wastewater with the help of magnetic separation.

During the photocatalytic dye degradation process using the C/PAni/IONP hybrid biocomposite, PAni sensitizes the IONPs in the visible region and the IONPs in return help the charge separation in PAni and facilitate the formation of superoxide and hydroxyl radicals. These superoxide and hydroxyl radicals attack, degrade, and mineralize the dye. The whole process is shown in Figure S3. As can be seen, because the conduction band of IONPs and the lowest unoccupied molecular orbital level of PAni are well-matched for the charge transfer, the electrons promoted from the π−π* absorption band of PAni upon natural light irradiation are easily injected into the conduction band of the IONPs while electrons in the valence band (VB) of the IONPs are transferred into PAni and left holes (h+) in the VB, which can yield superoxide and hydroxyl radicals on the surface and at the interface of IONPs and PAni/IONP, respectively, leading to the enhanced catalytic activity.

The oil absorption and removal ability of the as-synthesized C/PAni/IONP hybrid biocomposite from the oil−water mixture is shown in Figure 7. As can be seen, the oil was completely removed from the oil−water mixture within 30 s of incubation (Figure 7a−d). A permanent magnet (~1000 Oe) was used to track the sample to absorb more oil from other oil-contaminated area. The sample pellet was withdrawn from the mixture using the permanent magnet and weighed to determine the oil absorption capability of the sample. It was found that the as-synthesized hybrid biocomposite powder exhibits an oil absorption capability up to 2.1 g/g, which is comparable to those of previously reported magnetic biocomposite materials and better than those of previously reported oil-absorbing composite powders. It is imperative to note that the oil absorption of the hybrid biocomposite is mainly due to the existence of IONP-stabilized collagen in the composite matrix, which has good oleophilic nature and porosity. The results show that the C/PAni/IONP hybrid biocomposite has a great potential for the absorption and removal of oil from the oil-contaminated environment assisted with magnetic separation.

Electromagnetic waves comprise both electric and magnetic fields at right angle to each other. EMI shielding is the attenuation of a propagating electromagnetic wave by blocking the fields with barriers made of conductive or magnetic materials. Hence, it is logical to employ a bifunctional material having both electrical conductivity and magnetic properties as a shield. When an incident electromagnetic wave attempts to pass through the shield, phenomena such as reflection, absorption, and transmission or multiple reflection may occur, which are due to the interaction with the charge carriers and magnetic dipoles of the shield (Figure 8a). Therefore, the total SE (SE_T) is the summation of contributions from absorption (SE_A), reflection (SE_R), and transmission or multiple reflection (SE_M). However, when SE_T > 15 dB for a single layer of the shielding material, then SE_M can be neglected (SE_T (dB) ≈ SE_A + SE_R). As can be observed in Figure 8b−d, the as-synthesized C/PAni/IONP composite exhibits total SE (SE_T) in the range from 22 to 25.6 dB at 8 GHz and from 20 to 21.5 dB at 12 GHz for the samples with thicknesses from 1 to 2 mm. It is evident that the SE of the C/PAni/IONP composite gradually increased as the sample thickness increases. It is also intriguing to note that the total SE of the sample is mainly due to the absorption component rather than reflection. The key mechanism of EMI shielding is typically reflection due to the interaction of the EM radiation with the free electrons on the surface of the shielding material. Absorption occurs when the electric or magnetic dipoles of the shield material interact with the electromagnetic waves. For higher magnetic permeability shielding materials, which provide a magnetic dipole, shielding by reflection decreases while the absorption component increases. Highly conducting materials such as carbon nanotubes shield majorly by reflection rather than absorption. Conversely, hybrid composite materials with magnetic and conducting properties impart EMI shielding predominantly by absorption. A similar mechanism is expected here as well for our C/PAni/IONP composite material because of its inherent bifunctional properties.

The return loss and SE of the C/PAni/IONP composite are shown in Table S2. Return loss is the transmission of electromagnetic radiation through the materials due to the increased impedance mismatch between the shield and free space. The high return loss results in a lower SE of the sample. It is observed that the C/PAni/IONP composite gradually reduces the return loss as the sample thickness increases. The results also show that the C/PAni/IONP composite exhibits average total SE values of 20.6, 21.7, and 22.8 dB at 1, 1.5, and 2 mm sample thicknesses, respectively, in the X-band frequency range (8−12 GHz). In general, a total SE value of 20 dB is required for laptops and desktop computers and other commercial electronic appliances. The SE value of 20 dB indicates that the shielding material is capable of blocking 99% electromagnetic radiation. Hence, the results demonstrate that the prepared C/PAni/IONP composite can be a potential candidate for the EMI shielding of commercial electronic appliances.

3. CONCLUSIONS

An electrically conductive and magnetically active hybrid biocomposite was synthesized using an in situ oxidative polymerization technique with the compositions of collagen, PAni, and IONP for heterogeneous applications. The prepared C/PAni/IONP hybrid biocomposite powder showed an excellent electrical conductivity and a saturation magnetization of 2.44 × 10−3 S/cm and 8.32 emu/g, respectively, with good thermal stability. The electrical conductivity of the hybrid biocomposite was demonstrated through a simple LED lamp and battery setup, showing a decent brightness, which indicates the less obstruction of current flow in the composite matrix. The prepared hybrid biocomposite exhibits a significant photocatalytic activity toward the degradation of methylene blue up to 81% within the period of 2 h. It also showed an effective oil absorption and removal from the oil−water mixture. This study also reveals that the C/PAni/IONP hybrid biocomposite exhibited an absorption-dominant EMI SE surpassing 20 dB in the X-band frequency range of 8−12 GHz at a minimum thickness of the sample. Hence, the prepared C/PAni/IONP hybrid biocomposite has potential for a wide range of applications such as biosensors, photocatalysis, oil absorption, and EMI shielding, thereby demonstrating a sustainable approach for the effective usage of biowastes.
4. EXPERIMENTAL SECTION

4.1. Materials. Trimmed wastes from cowhide were obtained from the pilot tannery at the CSIR-Central Leather Research Institute, Chennai. Aniline, ferric chloride (FeCl₃), ammonium persulfate (APS), ferrous sulfate (FeSO₄·7H₂O), anthraquinone-2-sulfonic acid sodium salt (AQSA-Na), trisodium citrate, and sodium hydroxide were procured from Sigma-Aldrich, India. All other reagents used were of analytical grade.

4.2. Synthesis of IONPs. The functionalized water-dispersible IONPs were synthesized according to the protocol of Wang et al. without employing any solvent. Briefly, 0.32 g of FeCl₃, 0.28 g of FeSO₄·7H₂O, and 0.5 g of trisodium citrate were blended thoroughly using a mortar and pestle. The delimited hide pieces were dehydrated in 35% rawhide trimmed pieces were soaked, limed, dehaired, relimed, and delimed as per conventional leather processing procedures. The delimed hide pieces were dehydrated in 35% acetone for 3 h, followed by 100% methanol each 3 h duration to completely remove the moisture. The collected functionalized IONPs were dried at room temperature and then ground to make a fine powder.

4.3. Synthesis of C/PAni/IONP Hybrid Biocomposite. The schematic of the synthesis of PAni and C/PAni/IONP hybrid biocomposite is shown in Figure 9. Briefly, the collected rawhide trimmed pieces were soaked, limed, dehaired, relimed, fleshed, and delimed as per conventional leather processing procedures. The delimited hide pieces were dehydrated in 35% and 70% acetone for 3 h, followed by 100% methanol five times each 3 h duration to completely remove the moisture. The solvent-dehydrated trimmed pieces were thoroughly dried in a vacuum drier and ground into powder using a Wiley Mill of 2 mm mesh size. About 10 g of the hide powder was weighed and blended in 500 mL of 0.5 M glacial acetic acid at 4°C.

From this solution, 100 mL of collagen was taken in a clean vial and stirred with different concentrations of aniline from 0 to 1 (weight ratios with respect to collagen) at room temperature for 30 min. Subsequently, a fixed 1:1 weight ratio of IONPs dispersed in deionized water was added dropwise to the collagen/aniline mixture under continuous stirring for 30 min at 35°C. A mixture of aqueous solutions of AQSA-Na dopant (1:1 molar ratio of dopant/monomer) and APS oxidant (1:2 molar ratio of oxidant/monomer) was added dropwise to the reaction mixture to initiate the polymerization process. The reaction mixture was kept under constant stirring at 6 ± 2°C for 4 h. After the completion of polymerization, the synthesized dark green C/PAni/IONP precipitates were collected and washed with distilled water three times. Finally, the collected C/PAni/IONP precipitates were freeze-dried into powder, measured for electrical conductivity, and stored. For further characterizations, the 1:1:1 weight ratio composition of the C/PAni/IONP hybrid biocomposite was selected based on its highest conductivity value, as shown in Table S1.

4.4. Characterization of the Constituent Materials and the C/PAni/IONP Hybrid Biocomposite. FTIR spectroscopic analysis of the as-synthesized collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite was carried out using a JASCO FTIR-4200 spectrometer. The samples were ground into powder, mixed with KBr, and pressed to form pellets. The pellets were analyzed in a single-beam mode with an average of four scans and 1 cm⁻¹ resolution. XRD analysis of the as-synthesized collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite was carried out using a Rigaku Miniflex (II) desktop diffractometer (Ni filtered with Cu Kα radiation with λ = 0.15418 nm) at the 2θ range of 10–80° at a scan speed of 4°/min and a sampling step of 0.02°. The TGA of the as-synthesized collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite was carried out using a PerkinElmer (TGA Q50, V20.6 Build 31) analyzer in the temperature range of 25–800°C. The heating rate was maintained at 20°C/min under the nitrogen flow of 40 mL/min. The structural morphology of the as-synthesized collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite was analyzed using an FEI Quanta 200 scanning electron microscope at an accelerating voltage of 20 KV in different magnifications. The samples were coated with gold using an Edwards E306 sputter coater before the analysis. The particle size of the PAni, IONP, and C/PAni/IONP hybrid biocomposite was measured using a Nanotrac wave IIG particle size analyzer (Microtrac). The magnetic properties of the as-prepared collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite were measured using a vibrating sample magnetometer (VSM, Lakeshore, 7407 model) at room temperature.

4.5. Electrical Conductivity of the Constituent Materials and the C/PAni/IONP Hybrid Biocomposite. The electrical conductivity of the prepared collagen, PAni, IONP, and C/PAni/IONP hybrid biocomposite was analyzed by a two-probe method using a Prestige 4.5 Digital Micro-Ohm meter (Prestige Electronics, Mumbai, India) at room temper-
The powder samples were compressed to circular pellets with a thickness of 3.0 ± 0.2 mm and a diameter of 2.5 cm before the analysis. The conductivity (σ) of the pelletized samples was calculated using eq 1.

\[
\text{Conductivity of the sample (S/cm)} = \frac{1}{\text{resistance of the sample (Ω)}} \times \frac{\text{thickness of the sample (cm)}}{\text{area of the sample (cm}^2)}
\]  

(1)

The electrical conductivity of the pure collagen, PANi, IONP, and C/PAni/IONP hybrid biocomposite was also demonstrated through the LED lamp and battery setup. The sample pellets were placed between the four alkaline batteries (LR41, 1.5 V each) and connected to an LED (5 mm length, 2.1 V) lamp unit. The illuminated LED lamp was photographed using a digital camera (Sony, Cyber-shot, DSC-WX200).

4.6. Photocatalytic Activity of the Constituent Materials and the C/PAni/IONP Hybrid Biocomposite. The photocatalytic activity of the prepared collagen, PANi, IONP, and C/PAni/IONP hybrid biocomposite was measured by the degradation of methylene blue under the irradiation of natural light condition. Briefly, 150 mg of the powder sample was immersed in 100 mL of methylene blue solution (10 mg/L) and stirred under the sunlight. At regular intervals, 1 mL of the reaction medium was taken to measure the degradation of methylene blue using the UV–vis spectrophotometer (UV-1800, Shimadzu). The absorbance of the characteristic wavelength of methylene blue was recorded, and its degradation percentage was estimated according to eq 2. The powder sample was recovered from the treated water using permanent magnets (~1000 Oe) utilizing the magnetic property of the biocomposite.

\[
\text{Methylene blue degradation (%) = } \frac{\text{initial absorbance } – \text{sample absorbance}}{\text{initial absorbance}} \times 100
\]

(2)

4.7. Oil Absorption and Removal Studies of the C/PAni/IONP Hybrid Biocomposite. Oil absorption and removal were carried out by immersing a known weight of the C/PAni/IONP hybrid biocomposite pellet (manually pressed to a cylindrical shape with 5 mm diameter and 4 mm height) into the mixture of distilled water and used motor engine oil. The oil-absorbed sample was tracked in the natural light condition. Briefly, 150 mg of the powder sample was immersed in 100 mL of methylene blue solution (10 mg/L) and stirred under the sunlight. At regular intervals, 1 mL of the reaction medium was taken to measure the degradation of methylene blue using the UV–vis spectrophotometer (UV-1800, Shimadzu). The absorbance of the characteristic wavelength of methylene blue was recorded, and its absorption percentage was estimated according to eq 2. The powder sample was recovered from the treated water using permanent magnets (~1000 Oe) utilizing the magnetic property of the biocomposite.

The conductivity values of the as-synthesized C/PAni/IONP hybrid biocomposite at different proportions of PANi, SEM image of the C/PAni/IONP hybrid biocomposite at higher magnification, VSM curves of collagen and PANi, schematic showing the dye degradation mechanism by the C/PAni/IONP hybrid biocomposite, and return loss (PDF)

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