Applications of Biodegradable Poly Blends/Composites

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Biodegradable poly(ε-caprolactone) (PCL) and its composites or blends have received a lot of attention in the past because of their potential applications in human life and environmental remediation. Greater efforts have been made to develop biodegradable chemical materials as adsorbents that do not pollute the environment in order to replace traditional materials.

polycaprolactone blend composite

1. Pollutant Removal Applications of PCL Blends/Composites

1.1. Dye Removal by PCL Blends

Some polymers, particularly those with efficient functional groups that are insoluble in water, have been employed as adsorption agents for the removing of dyes and heavy metal ions. Polymers' ability to remove pollutants is determined not only by their active functional groups, but also by their structure, surface area, and porosity. Because of its limited adsorption capacity, low mechanical qualities, and water-insoluble hydrophobic features, pure PCL is ineffective as an adsorbent. Because of these poor qualities, polymer blends or composites of PCL have been employed as excellent adsorption agents for the elimination of dyes from aqueous solution in place of pure PCL. Blending a hydrophobic polymer (PCL) with functional polymers, such as cellulose, chitin, chitosan, lignin, and alginate, at varying ratios is significant for enhancing adsorption active sites and lowering costs. When compared to other polymer classes, polymer nanofibers offer unique features, like high water permeability, high porosity and surface area. As a result, converting ε-caprolactone polymers into PCL fibers can be another successful approach for dye removal [1].

For instance, Guo et al. fabricated novel composite fiber adsorption materials with different mass ratios consisting of PCL and beta-cyclodextrin-based polymer (PCD) by electrospinning. The fiber materials obtained showed exceptional elective adsorption for MB and 4-aminoazobenzene (AAB) solutions. Addition of a PCD constituent to composite fibers improved the mechanical resistance (breaking stress 3.41 MPa for PCL/(50%)PCD) of membranes and altered the sorption uptake because of the molecular structure of the cavity through host–guest interaction. The specific surface area values rose substantially along with increasing of PCD constituent in the composite fibers, reaching 11.5 m^2/g for PCL/(50%)PCD composite fibers (7.50 m^2/g for neat PCL fibers), suggesting the development of additional anchoring sites aiding the subsequent adsorption of dye compounds. The dye removal efficiency reached from 7.44 mg/g to 24.1 mg/g for AAB and from 3.89 mg/g to 11.2 for MB. Because of the excellent stability and selectivity of the adsorption process, the currently produced beta-cyclodextrin-based composite fibers (average diameter of 200–400 nm) have shown potential large scale uses in dye capture and wastewater remediation [2].

Many investigations are being conducted to find effective and ecologically acceptable techniques for degrading phenols and their derivatives. In order to create novel types of biocatalytic systems capable of removing bisphenol A, an attempt was made to generate PCL-chitosan electro-spun materials for tyrosinase immobilization. SEM scans validated the shape of the fibers and enzyme deposition. After enzyme deposition, fiber diameter increased significantly from 344 ± 121 nm to 689 ± 365 nm, demonstrating enzyme adhesion to the fiber surface. The constructed system was used in batch tests including the biodegradation of bisphenol A under different remediation circumstances. Over 80% of the pollutant was eliminated after 120 min of processing at temperatures ranging from 15 to 45 degrees Celsius and pH levels ranging from 6 to 9, using solutions containing up to 3 mg/L. After 30 days of storage, the immobilized biomolecule tyrosinase retained around 90% of its original activity (60% for free enzyme) and was still capable of removing more than 80% of bisphenol A, even after 10 repeated usages [3].

Chitosan-based nanofibrous membranes for dye adsorption from solution were created using hybrid electrospinning of chitosan (CS) and PCL or PCL-block-poly(ethylene glycol) (PCL-b-PEG or abbreviated as P) amphiphilic copolymers. PEG segments were shown to be capable of controlling the secondary fiber and core-shell structure. The addition of PEG component enhanced the compatibility of PCL and CS, decreased CS loss because of intermolecular hydrogen bonds formed between CS and PCL-b-PEG copolymer, and increased membrane stability. The adsorption studies revealed that the anionic CR dye adsorption process on CS-based membranes fits well with the pseudo-second order and the Langmuir isotherm models. The CS-based membranes (CS/P_{5K}, diameter of ~807.89 nm) with a PEG molecular weight of 5 kDa had high reusability, with highest adsorption capacity of 291.55 mg/g computed using the Langmuir model. The CS/P_{5K} removal effectiveness was maintained at 90.18% and dropped to 80% after 10 repetitions, demonstrating that the CS/P_{5K} nanofibrous membrane can be reused for dye removal. As a result, CS/PCL/PEG nanofibers appear to be promising membranes for water purification [4].

Amphiphilic PCL-PEG-PCL/Bentonite A2 nanocomposites were synthesized by in situ ROP of ε-CL in the existence of PEG chains, catalyzed by an intercalated Algerian Bentonite tetrabutylammonium hydrogen sulfate (TBHSA) (A1). For this purpose, sodium cations in bentonite were exchanged by tetrabutylammonium cations $[(C_4H_9)_4N^+]$. The XRD and transmission electron microscopy (TEM) measurements revealed that the silicate sheets in the PCL-PEG-PCL/layered silicate nanocomposites were partly exfoliated. The nanocomposite (A2) was employed to efficiently remove MB dye from aqueous medium. As the mass of the nanocomposite rose, so did the dye's adsorption capacity, which reached an ideal value of 0.13 g adsorbent at pH = 6.8. Calculating an adsorption capacity (q_{max}) of 600 mg/g within 90 min, the Langmuir isotherm provided the best match [5].

Karagöz et al. designed and manufactured electro-spun PCL nanofibers (NFs) adjusted with TiO_2 and Ag NPs. The as-prepared PCL/TiO_2-Ag NFs mats were created using one-step electrospinning and used for three separate applications: (a) reusable surface-enhanced Raman spectroscopy (SERS) substrate for non-qualitative analysis to track pollutants, (b) photocatalyst for organic pollutant degradation, and (c) antibacterial agent to kill bacteria. For the detection of MB dye, PCL/TiO_2-Ag NFs performed as a highly efficient SERS platform with a detection limit of 10 nM (MB). The photocatalytic degradation of the probe analytes MB under UV irradiation was completed in less than 180 min with degradation efficiency 93–95% using a PCL/TiO_2-Ag NFs nano-catalyst [6].

A membrane having a greater hydrophilic nature is predicted to be more fouling resistant. The biodegradable nature of PCL and the anti-fouling property of TiO_2 were combined in a composite and used in the construction of water purification membranes. TiO_2 nanoparticles' strong association boosted the stiffness of the supramolecular polymeric chain and improved the thermostability of the composite membranes. Porosity and pore size must also be evaluated to establish the membrane's appropriateness for separation applications. To promote pore development in the membranes, PEG is supplemented to the polymeric solution. The tensile strength of the membranes (2.5 N/mm^2) was increased by combining PEG with PCL and including TiO_2 nanoparticles. The optimal PEG and TiO_2 compositions were 6.24 and 1.0 wt% in PCL-TiO_2-PEG membrane, respectively. After bovine serum albumin filtering, the anti-fouling property of TiO_2 gave rise to roughly 90% flux recovery for the PCL-TiO_2-PEG membrane when compared to the PCL-PEG membrane. For membranes in water remediation uses, the PCL-TiO_2 combination would be a superior option [7].

Immobilization of particular bacteria onto electro-spun nanofiber webs of PCL was used to create innovative bio-composite materials. After adequate numbers of bacteria were immobilized on electro-spun nanofiber webs, equivalent web samples were used to evaluate their ability to remove the Setazol Blue BRF-X dye. Both PCL/bacteria and PLA/bacteria webs eliminated the Setazol Blue BRF-X dye within 48 h at each dose investigated (50, 100, and 200 mg/L), and their removal efficiency (87.88% and 89.57% for 50 mgL^{-1} of dye concentration) were extremely similar to free bacterial cells. The samples' Q_{eq} values were in the same order: 119.56 $mg \cdot g^{-1}$ for free bacteria, 109.75 $mg \cdot g^{-1}$ for PCL/bacteria web samples, and 112.15 $mg \cdot g^{-1}$ for PLA/bacteria web samples. The bacteria immobilized webs were then evaluated for five reuses at starting dye concentration of 100 mg/L and found at the end of the test to be potentially reusable (removal capacity of PCL/bacteria:95.36%), with higher bacterial count immobilization and faster removal of dyes. Overall, their findings indicate that electro-spun nanofiber webs are viable platforms for bacterial integration and that webs immobilized with bacteria can be employed as starting inoculants for the removal of textile dyes from an aqueous medium [8].

Polydopamine (PDA) nanoparticles have a high adsorption capacity and can be utilized as an adsorbent. On the other hand, nano-sized PDA adsorbents are prone to aggregation and so have severe limitations in the adsorption field. To address this issue, Wang et al. produced the PCL/PEO copolymer by electrospinning and blended it with PDA. They discovered that modifying the surface and porosity of the produced nanofibers enhanced their adsorption capability. The PCL/PEO@PDA composite illustrated a high number of active sites for MB and MO adsorption. It is important to note that the PCL/PEO@PDA-45 composite as an adsorbent showed a better matched adsorption capacity for the anionic dye MO (60.22 $mg \cdot g^{-1}$) than that of the cationic dye MB (14.85 $mg \cdot g^{-1}$). Furthermore, the PCL/PEO@PDA blends were reusable numerous times and performed well as adsorbents. The removal effectiveness of the PCL/PEO@PDA adsorbent on MO dye reduced from 99% to 93% after eight reuses, confirming the adsorbent's outstanding stability and recyclability [9].

Self-assembly nanohybrid structures GO@PCL, CNT@PCL, and GO-CNT@PCL were produced by a wet electrospinning-aided method with a three-dimensional fibrous PCL network surrounded by graphene oxide (GO) layers on which carbon nanotube (CNT) brushes were stuck [10][11]. They studied the influence of surface chemistry on the sorption ability of fluffy scaffolds' nanohybrid materials towards water soluble organic dyes, such as MB and MO. Given that such a cationic MB dye may interact with aromatic and oxygenated areas of composites, all of the compounds perform quite well in terms of MB removal. GO-CNT@PCL outperformed the other nanohybrid samples, with a sorption capacity of 400 $mg{\cdot}g^{-1}$ and an elimination efficiency of almost 100%. In the instance of MO removal, GO-CNT@PCL demonstrated 100% effectiveness with more than 80 $mg{\cdot}g^{-1}$ adsorption in 6 h, likely due to the combination of wettability by GO and the amount of active sites by CNTs [10].

Three PEG/PCL copolymers were prepared with various topologies but the same mol ratio of PEG to PCL. Different techniques were used to characterize these compounds, which included di-block (Di-PEG-PCL), tri-block (Tri-PEG-PCL), and multi-block (Multi-PEG-PCL) copolymers. The influence of topology on the efficiency of MB removal from aqueous medium was researched. The multi-block copolymer outperforms other topologies in terms of adsorption efficiency. The regression coefficient data showed that the Freundlich isotherm (R^2= 0.9840) accurately describes the MB adsorption by copolymers [12].

1.2. Dye Removal by PCL/Metal Oxide Composites

Metal oxides have been added to PCL to improve dyeability, thermal stability, adhesion, and other properties. Because it is miscible with a wide range of metal oxides, flexible, biocompatible, and mechanically suitable, it has the exceptional ability to enhance the characteristics of other materials, which results in a wide range of applications.

The electrospinning method was used to create high surface area porous PCL membranes containing Fe_3O_4 nanoparticles. In the existence of H_2O_2 and UV light, they were tested as degradation catalysts in Fenton reactions to break down cationic MB dye. The results showed that the fiber catalyst system (fiber diameter: 713 ± 139 nm for 15% PCL) performed well in terms of MB removal (99% MB) and was functional after six cycles (96% MB). PCL membranes may interact strongly with organic compounds because of their hydrophobic surfaces. The excellent catalytic properties of the composites are attributable to the synergy of the porous surface (pore size spans from 2.43 to 6.56 μm) and the implanted Fe_3O_4 nanoparticles. It also has the benefit of being environmentally safe and readily separated without the use of an external magnetic field [13].

PCL nanofibrous membranes integrated with hydroxyapatite (HAP) adjusted with varying concentrations of Cu(II) ions were created. A variety of spectrometric, microscopic, and surface science methods were used to describe the architectures, morphologies, and surface roughness of the built (Cu-HAP@PCL) membranes. Examination of the surface morphology showed that these membranes present as web fibers with different diameters ranging from

0.45–1.5, 0.45–1.21, 0.21–1.5, 0.3–1.1 to 0.2–0.9 µm; however, the average roughness increased exponentially with increasing Cu(II) ion content. The maximum degradations of MB dye were achieved after 70 min of visible light irradiation utilizing the constructed Cu-HAP@PCL membranes, with values of 88.6%, 89.4%, 91.0%, 91.1%, and 94.3%. The degradation mechanism can be summarized by the following reactions.

$$[Cu_xCa_{1-x}(PO_4)_6(OH)_2] + h\nu \rightarrow e^-(CB) + h^+(VB)(1)$$

$$[Cu_xCa_{1-x}(PO_4)_6(OH)_2] + H_2O + 2e^- \rightarrow 2OH^- + Cu(2)$$

$$e^- + O_2 \rightarrow O_2{}^{*-}(3)$$

$$e^- + O_2{}^{*-} + 2H^+ \rightarrow H_2O(4)$$

$$2e^- + HO_2{}^{*-} + H^+ \rightarrow OH^* + OH^-(5)$$

$$MB + OH^* \rightarrow MB(degenerated) + CO_2 + H_2O(6)$$

Hydroxyl ions (OH*) and superoxide scavengers ($O_2{}^{*-}$) are the most efficient ions in the destruction of MB dye. Because these ions have a strong chemical activity while interacting with MB molecules, small fragments of molecules may be formed [14].

Elias et al. investigated the efficiency of a PCL–organically modified montmorillonite clay (Cloisite 10 A) nanocomposite membrane in the removal and degradation of rhodamine B from aqueous systems under VIS light (50 W). A nanocomposite containing nine by weight of Cloisite 10 A effectively converts rhodamine B into environmentally friendly products in less than 3 h. C10A’s adsorptivity and -OH groups on the surface promote electron-hole pair separation and improve photocatalytic activity [15].

Geravand and colleague [16] developed a biodegradable membrane made of PCL/MXene nanosheets ($Ti_3C_2(OH)_2$). Using hydrophilic MXene as the nanofiller resulted in significant improvements in biodegradability, water permeability, and anti-fouling characteristics. The findings demonstrated that the PCL membrane combined with 4 wt% MXene displayed the maximum hydrophilicity and pure water permeance (PWP), which were nearly four times higher than those of the neat PCL membrane (5.99 vs. 1.43 L/m^2.h.bar). Furthermore, the membrane containing 1% MXene exhibited 98.92% rejection of crystal violet ((CV) = 50 ppm). All three mechanical features improved with rising the MXene concentration to 3wt% (elastic modulus from 19.87 ± 0.07 to 36.61 ± 0.52 MPa, tensile strength from 5.14 ± 0.27 to 10.51 ± 0.33 MPa, and elongation at break from 316 ± 6 to 359 ± 7%), but declined with a continual rise in MXene concentration. The mechanical performance of membranes was affected by a variety of parameters, including MX distribution uniformity, polymer aggregation, and augmented membrane porosity [16].

As photocatalytic materials, neat TiO_2 nanoparticles (TiO_2 NPs) have limited reusability. To achieve effective photocatalysis, certain high surface area supports are added to the TiO_2 loading. Porous electro-spun PCL fiber mats were utilized in the study to support the capacity and dispersion of TiO_2. The porous PCL mats can provide a broad contact surface area for excellent TiO_2 photocatalytic activity. Furthermore, the inclusion of rectorite (REC) might lower fiber diameters, induce stabilization of the anatase phase, and increase specific surface area, which could be favorable to photocatalysis. More notably, REC improved the performance of porous PCL/TiO_2 mats, resulting in high photocatalytic degradation. The findings suggested that porous PCL/TiO_2/REC mats might be good photocatalysts for the degradation of organic dyes like Rhodamine B. After 3 h, the crimson solution turned translucent while the mats became red. At the end of the experiment, the photocatalytic activity of TiO_2 NPs and fibrous mats all achieved 98%. In the first 45 min, the photocatalytic effectiveness of PCL/TiO_2/REC mats was greater than that of neat TiO_2 NPs, confirming that REC expedited the photocatalytic process [17].

The solution casting approach to create TiO_2 nanoparticle embedded polymer films from two biodegradable polymers such as cellulose acetate (CA) and PCL was used. The photo-degradation rate rose with rising content of TiO_2 NPs in CA and PCL films. TiO_2-PCL films had the highest photocatalytic efficiency of the two types of polymer materials tested. After 3 h of UV-A light exposure, PCL film combined with 5% TiO_2 had the greatest MB degradation rate (72%), followed by 5% CA film, with 53% dye degradation. As a result of the significant quantity of NPs around the pores and cracks on the film, the porous structure of TiO_2 in PCL-TiO_2 film could produce high MB degradation [18].

Solution casting was used to create the PCL and Fe_2O_3/PCL nanocomposites sheets/films. The morphological analysis revealed that the Fe_2O_3 nanoparticles (250 nm) were well disseminated and lodged inside the PCL matrix. The thermal stability of Fe_2O_3/PCL was poorer than that of pure PCL, which might be attributed to the activity of Fe_2O_3 as a catalyst in the thermal degradation of PCL. According to the DSC investigations, the crystallization temperature of the Fe_2O_3/PCL was somewhat higher than that of pure PCL. The polarized optical microscopy studies revealed that the size of Fe_2O_3/PCL spherulites was less than that of pure PCL. The UV-Vis spectra demonstrate that, as the irradiation period and the number of Fe_2O_3 nanoparticles in the nanocomposites increase, so did the photodegradation of rhodamine B (RhB) dye. Within 2 and 10 h, pure PCL photodegraded between 24 and 72% of the RhB dye, while Fe_2O_3 (6 wt%)/PCL composites degraded around 72 and 98% of the dye, respectively [19].

A simple hydrothermal approach was used to create hydroxyapatite (HAP) nanorods that were hydrophobically modified using lauric acid (LA). Pickering emulsion template technique was used to load HAP compound modified by LA (RHAP) and magnetite (m, Fe_3O_4) NPs as emulsifiers on PCL microspheres. The structure, constituents, and morphology of synthesized pure HAP nanorods (hydrophilic, water contact angle 11.7°) and m-RHAP-PCL microspheres (hydrophobic, water contact angle 111.3°) were analyzed by XRD, SEM, FTIR, and TGA. MG was used as a model dye to study the adsorption capability of m-RHAP-PCL microspheres. The highest adsorption capacity (q_{max}) of m-RHAP-PCL was 609 $mg \cdot g^{-1}$, and its relative adsorption performance was greater than that of pure HAP, showing that it has better MG adsorption potential. The values of R_L (from 0.157 to 0.263, which were much smaller than 1) and 1/n (0.204–0.290, which were less than 0.5) suggested that the adsorption process had occurred on its own. Moreover, the adsorbent recovers easily in magnetic fields and its ability to remove MG remains unchanged over four cycles, demonstrating the reusable nature and stability of the m-RHAP-PCL adsorbent for MG sorption [20].

A mat of graphene oxide (GO) nanosheets was employed to dope fine powder of magnetite nanoparticles (MNPs) with varying amounts of copper ions (Cu(II)). These compositions ($Cu_xFe_{3-x}O_4$/GO) were fully integrated into PCL electro-spun nanofibrous membranes. The morphological characteristics of the membranes revealed that diameters were varied with Cu(II) ions variation, starting at 0.35–1.06 µm and 1.8–3.9 µm without Cu, being 0.19–0.45 µm and 0.75–1.42 µm for the greatest contribution of Cu, while GO scattered grains of 0.56–1.5 µm were observed. The toughness at the highest additional dopant was 4.69 ± 0.29 MJ/m^3, while the tensile strength was adjusted to around 8.96 ± 0.45 MPa. These nanofiber membranes' ability to capture MB dye from aqueous medium was also tested. The created nanofiber membrane could absorb 95.1% of the MB after 36 min of contact time, and the composition was still stable after five removals, with a performance of about 90.1% for the 0.8Cu-MNPs-GO@PCL [21].

The hydrothermal method was used to synthesize PCL/CA/$MnWO_4$ nanocomposite film. SEM, XRD, FTIR, UV-DRS, and XPS were used to investigate the morphology, chemical composition, optical, and molecular bonding properties of nanocomposite. Photocatalytic activities of $MnWO_4$ and CA/PCL/$MnWO_4$ nanocomposites on crystal violet (CV) dye were investigated and found to be 76.02% and 82.29%. Furthermore, these nanocomposite films showed significant efficiency and stability in the removal of CV dye, with only a small performance decline even after three cycles of repetitive use. The enhanced photocatalytic performance was attributed to the reduction in the band gap caused by the strong surface interaction between PCL/CA membrane and $MnWO_4$. These results indicated that PCL-based photocatalyst could be a promising candidate for photocatalytic dye degradation processes [22].

Ring-opening polymerization was used to create a PCL/Fe_3O_4 magnetic nanocomposite (PCL/Fe_3O_4 MNC). Then, as a new adsorbent, PCL/Fe_3O_4 MNC was utilized to capture remazol brilliant violet 5R (RBV 5R) from aqueous solution. The response surface methodology (RSM) was employed to maximize the adsorption procedure and define the optimum conditions. At a contact time of 168 min, a PCL/Fe_3O_4 MNC amount of 0.40 g and an RBV 5R concentration of 7.18 mgL^{-1}, 95.40% RBV 5R removal was obtained. ATR tests revealed that the chemical bonding in PCL/Fe_3O_4 MNC did not change significantly before and after the adsorption method [23].

PCL composite was used not only for dye removal but also for oil separation. By incorporating SiO_2 aerogel, exceptional superhydrophobic PCL membranes with an alternating hierarchical micro-nanometer structure were created. When the SiO_2 aerogel content in the PCL membrane was 0.5% (PCL/SiO_2-a0.5), the maximum water contact angle (WCA) of 166.8 ± 1.5° was acquired, which was greater than other published polymer-based membranes. The surface energy of the PCL membrane was reduced by SiO_2 aerogel. The internal structure of the PCL/SiO_2-a0.5 membrane, which was made up of micro-nano spheres and fibers, increased the porosity of the membrane, allowing for more adsorption area for water-in-oil separation. In the meantime, the PCL/SiO_2-a0.5 membrane demonstrated exceptional chemical stability, self-cleaning ability, and reusability [24].

Uzunok and Sönmez improved the hydrophobicity of PCL by incorporating different silane-based cross-linkers such as tris [3-(trimethoxy-silyl)propyl] iso-cyanurate, tetraethyl orthosilicate, and 1,8-bis(triethoxy-silyl)octane for the removal of oil from an aqueous system. The obtained sorbents showed high and quick absorption properties in the range of 5450–51,000 $mg{\cdot}g^{-1}$. After 10 cycles of oil sorption, the sorbents demonstrated high oil sorption capacity and reusability without any loss [25].

PCL blends/composites have an important place not only in dye and heavy metal removal, but also in oil cleaning. The use of oil-soaked adsorbents in the recovery and clean-up of oil spills is gaining importance day by day. Recently, magnetic nanoparticle (MNP)-based absorbers have attracted interest as a new method both to treat oil spills and to reduce the amount of labor required. Eom et al. performed the synthesis of MNP embedded PCL adsorbent, which can be collected easily under a magnetic field and has oleophilic and environmentally friendly properties. MNP embedded PCL adsorbent (MNP/PCL) exhibited perfect Arabian light (AL) crude oil absorption capacity (45.7 g/g) and reduced the absorption time of oil-immersed sorbent because of its electro-spun structure. In the future, such sorbents may be applicable in large scale oil spill projects [26].

1.3. Heavy Metal Removal by PCL Composites/Blends

PCL is one of the promising compounds for manufacturing biocompatible membranes due to its outstanding structure and superior mechanical and physical features. PCL nanocomposites have also found usage in removing heavy metal ions from aqueous system. Bio-nanocomposite CD-PCL-TiO_2 was utilized as an adsorbent material in removing of Pb(II) ions from wastewater after a two-step process of sol gel synthesis of TiO_2 particles and polymer solution blending. The highest removal of Pb(II) ions was 98% at pH 9.7, concentration 10 ppm, and dosage of 0.005 g. This method has a significant advantage since it does not introduce any secondary pollutants into the treated water [27].

Liakos et al. mixed the solutions of 8.42% by weight PCL in dichloromethane with sodium alginate (SA) (5, 10, 15, 20, 25 or 30% by weight based on PCL) and the resulting films were placed in a heat extruder to form PCL/SA filaments.

Electrospinning was used to create nanostructured membranes of cellulose acetate (CA) with varying PCL loadings (0%, 10%, 20%, and 30%) in removing of Pb^{2+} ions from aqueous medium. Using instrumental techniques revealed that the introduction of PCL into CA resulted in a finer fiber radius, increasing the membrane's surface area and thus increasing the number of adsorption sites. According to the findings, Pb^{2+} ion adsorption capacity was increased from 43.96 $mg{\cdot}g^{-1}$ of pristine CA membrane to 70.50 $mg{\cdot}g^{-1}$ of CA/10%PCL filled membrane. Furthermore, the findings of this experiment agreed best with the pseudo second-order kinetics and Freundlich isotherm, both of which accurately described the adsorption process [28].

Coaxial electrospinning was used to create core-shell-structured CA-PCL/CS nanofibers with outstanding hexavalent chromium (Cr(VI)) removal performance. In an acidic environment, the influence of the core/shell ratio on the adsorption ability was investigated. The findings demonstrated that, when compared to the CS powder adsorbent, all core-shell-structured fibrous material demonstrated improved adsorption and durability. CA-PCL/CS fibrous material with a core/shell ratio of 0.442 absorbed 126 mg·g^{-1} of Cr(VI) ions at RT. Adsorption kinetics showed that chemisorption was the rate-limiting step due to significant electron transfer, sharing or exchange between CA-PCL/CS nanofibers and Cr(VI) ions [29].

Benhacine et al. combined PCL with silver montmorillonite (Ag-MMT) to produce nanocomposite membranes. SEM analysis revealed that the synthesized membranes had homogeneous sponge microstructures. Gradual incorporation of nanoparticles (2, 3, and 5 wt%) into the PCL matrix resulted in a significant increase in membrane thickness. The authors of the current study administered the treatment to actual wastewater samples and documented a decrease in the concentrations of nitrates by 15.12% and sulphates by 45.61%, along with significant reductions in the levels of Pb, Zn, and Cd, by 41.38%, 53.57%, and 61.11%, respectively [30].

Irandoost et al. prepared nanofiber nanocomposite of PCL adsorbent modified by binary fillers such as nano-clay and zeolite clinoptilolite NPs to improve the adsorption properties. Lead removal studies have shown that each component in the nanofibrous adsorbent has a synergistic effect on the Pb(II) adsorption capacity (19.92 mg/g). In thermodynamic studies, negative ΔG values (between −0.173 and −3.003 kj/mol) indicated spontaneous Pb(II) adsorption at all temperatures and concentrations [31].

1.4. Adsorption Mechanism of Dyes/Metal Ions onto PCL Composites/Blends

Water-insoluble homo-PCL polymers are not very effective against environmental pollution, such as heavy metal ions and dyes, due to their low adsorption efficiency, low pore volumes, low pore sizes and high hydrophobic properties. Instead, PCL blends/composites are preferred as effective adsorbents for removing dyes and metal ions from an aqueous medium [32][33]. The blend of a polymer including functional groups with a hydrophilic polymer, like cellulose, chitosan, and chitin. in various ratios is crucial for enhancing hydrophilicity, raising adsorption active sites, and decreasing cost. Understanding the adsorption mechanism of dyes or heavy metal ions on PCL adsorbents is critical for optimizing the adsorption method and improving the efficiency of PCL nanofibers in dye removal. The adsorption of dyes or metal ions on the surface of nanofiber materials is controlled by solution conditions (such as pH and temperature), nanofiber nature (like porosity, area of surface, functional moieties, and surface morphology), and dye nature (like neutral, cationic, and anionic forms, and molecular size of dyes) [34][35]. The adsorption mechanism may be unclear due to the variety of factors influencing dyes or metal ions' adsorption onto the surface of nanofibrous. It is essential to carry out isotherm, kinetic, thermodynamic, and spectroscopic studies, in addition to looking at the impact of pH, in order to gain a clear and comprehensive understanding of the adsorption mechanism. According to various studies [36][37][38], dyes' or metal ions' removal from effluents using pure PCL, PCL blends, and PCL composites are most likely accomplished through hydrogen bonding, van der Waals (VDW) forces, stacking, hydrophobic interactions, electrostatic interactions, and pore filling. The interactions are influenced by the type of functional moieties on the surface of PCL nanofibrous, their morphology, and the type of filler added to the nanofibrous. These interactions, which operate concurrently to varying degrees, can be utilized to explain the adsorption mechanism of dyes and metal ions [1][39][40][41].

Draoua et al. investigated the MB dye removal adsorption performance of a PCL–PEG–PCL/Bentonite nanocomposite [5]. They came to the conclusion that the sorption mechanism was dependent on the hydrophobic interaction between the dye and the copolymer's hydrophobic block (PCL), as well as the electrostatic interaction between the surface (the SiO- and AlO-) and the edge moieties of bentonite and the dye's sulfonic group.

Alrafai et al. [14] studied the degradation mechanism of MB on the surface of PCL nanofiber membranes associated with hydroxyapatite (HAP) doped with varying quantities of Cu(II) ions (Cu–HAP@PCL). The degradation efficiency of MB dye on the fabricated Cu–HAP@PCL membranes indicated that the maximum degradation of 94.3% was accomplished after 70 min exposure to visible light. They discovered that the degradation efficiency was primarily increased by increasing the Cu contribution and lengthening the irradiation time [14].

Chen et al., for example, used FTIR and XPS techniques to investigate the adsorption mechanism of CR dye on the surface of the CS/PCL-b-PEG/SA@PDA membrane. They came to the conclusion that dye adsorption was accomplished through a combination of interactions, like hydrophobic interactions, hydrogen bond interactions (between the adsorbent's amine and hydroxyl groups and the CR's sulfonate groups), and adsorption space on the porous membrane [42].

Pekdemir et al. suggested that there are two possible mechanisms for dye adsorption on the adsorbent surface, which are chemical and physical interactions between the dye compound (RBV-5R) and the polymer (PCL/Fe_3O_4) nanocomposite. The hydrogen bonding, π–π interactions, and VDW interactions between the adsorbing agent and the dye compound were thought to control the adsorption rate in the model [23].

Hussain et al. crosslinked tannin (TA)-reinforced 3-aminopropyltriethoxysilane (APTES) with PCL fabricated via electrospinning and investigated the colorimetric performance of membrane for $Fe^{2+/3+}$ ions. They discovered that Fe ions bind to the crosslinked composite membrane due to FeTA complexation to form PCL-FeTA-APTES. According to the results of adsorption filtration, PCL-FeTA-APTES membrane was reusable and had higher MB dye adsorption (32.04 mg·g^{-1}) than PCL-TA-APTES membrane (14.96 mg·g^{-1}).

Lee et al. prepared coffee/PCL composite filters from coffee grounds and PCL and utilized them to eliminate Cu(II) ions from an aqueous system [43]. They discovered that, for 50 and 100 M Cu(II) ions, the removal efficiency of coffee/PCL composites was 96.6% for 4 h (q_{max} = 25.91 mg/g). All the samples' adsorption processes exhibited both monolayer and multilayer adsorption characteristics. The adsorption of Cu(II) ions was attributed to the strong binding or interaction between adsorbent and adsorbate.

In the study of Ramírez-Rodríguez et al., the hybrid membrane of PCL-whey protein isolate (PCL-WPI) adsorbed a significant amount of Cr in just under 60 min because of the abundance of adsorption sites on the adsorbing agent surface. However, the adsorption of Cr dropped significantly with time because of occupation of the active sites of the membrane, and adsorption equilibrium was reached after 3.5 h [44].

The dynamic elimination of arsenic from an aqueous medium with an adsorption membrane composed of an iron-intercalated montmorillonite-filled PCL matrix (Fe-MMT/PCL) was performed by Pena et al. [45]. According to parametric studies, longer breakthrough times were associated with a low flow rate (20 $mL\cdot min^{-1}$), a low starting inlet concentration (2 ppm), and a thick nanofiber membrane (0.75 mm).

Composite membranes with functionalized fillers have being investigated for selecting adsorption. Carbon Quantum Dots-Polyacrylonitrile(PAN)/PCL nanocomposite membranes were prepared by electrospinning and were designed for Cu(II) adsorption. The maximum adsorption capacity of a nanofiber mat with respect to contact time was 63.45 $mg\cdot g^{-1}$, with a highest adsorption efficiency of 90.74%. CQD in PAN and PAN/PCL membrane magnified the fiber size distribution from 50–100 nm to 150–250 nm, increasing the hydrophilicity of the PAN/PCL membrane. The physical adsorption method, which involves VDW forces and hydrogen bonds between adsorbent and adsorbate, governs the adsorption behavior [46].

The surface chemistry of the cellulose acetate (CA)/PCL electro-spun fibers immobilized with the novel mercury-favored organic dye (NF06) sensor was discovered to effectively facilitate the sensor’s fluorescence resonance energy transfer (FRET). Following Hg(II) chelation, both mobile and immobilized NF06 carried out FRET via a ring-open mechanism. Since the thiorhodamine-6 G acceptor stayed in a cyclic spirolactam in the lack of Hg(II), the FRET process was found to be inhibiting. However, due to the favorable electrostatic interactions between Hg(II) and the N- and S-atoms of NF06, an NF06:Hg(II) complex could easily form once Hg(II) was present. Consequently, the thio-R6 GH evolved from a ring-closed to a ring-opened spirolactam version [47].

2. Biomedical Applications of PCL Blends/Composites

2.1. PCL Blends/Composites for Tissue Engineering

PCL’s surface roughness and hydrophilic adjustability supplies preferred surface and interfacial features for the tissue. The degradation of materials utilized in the manufacture of scaffolds for tissue engineering implementations is an important property. PCL degradation is affected by molecular weight, shape, residual monomer content, autocatalysis, and other factors. Generally, it takes 2–3 years for PCL to completely degrade in the tissue fluid, which is constantly changing in the biological environment. In tissue engineering, the rate of material degradation is expected to be similar to the rate of tissue regeneration. When degradation is slower than the rate of tissue regeneration, it impedes tissue growth; when it is faster, it causes the linkage between tissue and scaffold to be lost, delaying the healing process [48].

Das et al. described a novel method for producing a PCL/chitosan structure including membrane products with double-porosity (macro=voids with interconnected microporous network) by chemically optimizing the solvent-containing and non-solvent phases and using a customized phase transition method. The existence of chitosan in the chitosan/PCL structure improved hydrophilicity significantly. The cytocompatibility of the chitosan/PCL scaffold was also investigated and found non-toxic. In the future, the blend membrane with dual porous morphology can be used for small radius vascular bypass uses. Surface macro=voids (20–90 μm) may be beneficial for three-dimensional cell adhesion and incrementation, while an interconnected microporous spongy network (7–20 μm) is anticipated to transport vital nutrients, oxygen, and growth factors between the macro-voids and the supernatant. All of these findings indicated that the chitosan/PCL nanofibrous structure would be a fantastic system for bone and skin tissue engineering [49].

Antioxidants are essential for the accomplishment of neural tissue regeneration and biomaterials with antioxidant action may be beneficial for peripheral nerve repair. To create an antioxidant bio-scaffold for nerve regeneration, Wang et al. used solvent-free ROP to create lignin–PCL copolymers. The lignin/PCL copolymers were then combined with PCL and designed into nanofiber scaffolds to support neuron and Schwann cell growth. The inclusion of lignin–PCL improved the mechanical features of PCL nanofibers while also providing good antioxidant characteristics (up to 98.3 ± 1.9% inhibition of free radicals within 4 h). These findings proposed that nanofibrous material containing lignin copolymers stimulated cell proliferation in both BMSCs and Schwann cells, increased Schwann cell myelin basic protein expression, and stimulated neurite outgrowth in dorsal root ganglion neurons. Overall, these long-lasting, naturally antioxidant nanofibrous materials could be a promising candidate for nerve tissue engineering uses [50].

The primary goal of Rezaei et al.’s work was the creation of a biologically and mechanically proper 3D printed scaffold for lung tissue engineering using a chitosan/PCL bioink. Design-Expert software was used to investigate different compositions for 3D printing. The scaffolds were tested for MRC-5 cell line growth, incrementation, and migration using chemical, biological, and mechanical methods. According to the findings, the average radius of the chitosan/PCL strands was 180 mm. Changes in PCL content had no effect on printability, whereas chitosan concentration did. The scaffolds demonstrated excellent swelling, degradation, and mechanical manner, but they can be altered by adjusting the PCL ingredient. In vitro, the scaffolds also demonstrated significant cell biocompatibility, non-toxicity, low apoptosis, high increment, and cell adhesion. To summarize, scaffold 3 (chitosan/PCL ratio: 4:1) demonstrated superior MRC-5 cell culture activity. As a result, this scaffold may be an excellent choice for lung tissue engineering [51].

There have been several attempts to combine biopolymers with inexpensive natural micro/nano particles, such as lignin, alginate, and gums to create new substances with improved features. The technique of electrospinning (ELS) was used to create nanocomposites of lignin and PCL scaffold. Nanocomposites containing (0, 5, 10, and 15% wt%) lignin were produced by adding lignin powder to the PCL solution with stirring at RT. When compared to pure PCL, the scaffold with 10% lignin had suitable porosity, biodegradability, minimal fiber radius, ideal pore size, and improved tensile strength and elastic modulus. Degradation tests using samples immersed in phosphate-buffer saline revealed that the addition of lignin could accelerate degradation of PCL composites by up to 10% [52].

2.2. PCL Blends/Composites for Wound Healing

PCL blends/composites are of great importance in the development and design of wound dressings that have antibacterial effects, absorb blood leakage and provide tissue regeneration in the rapid healing of wounds. By film casting, Kotcharat et al. created a PCL/bacterial cellulose (BC) composite with a specific ratio of 1%, 5%, 10%, 20%, 30%, and 50% *v*/*v* of BC. Alkaline purification was used to extract BC from nata de coco. The percentage of crystallinity decreased with increasing BC content. Porosity was discovered in the microstructure of the BC/PCL composite. It was noteworthy that the thermal decomposition manner remained stable up to 400 °C. When BC was added to DI water and phosphate-buffered saline (PBS) solution, there was no significant change in swelling manner. Swelling and degradation features were studied for 6 h and 4 weeks, respectively. As a result, PCL and BC-based composites can benefit significantly as exceptional candidates for wound dressing applications [53].

From a blend solution of PCL, cellulose acetate (CA) and dextran, an electro-spun nanofibers mat for use in wound dressing was favorably created. The composite mat's antimicrobial activity, blood clotting capacity, cell attachment, and cell increment were all improved by the addition of a small quantity of the antibacterial medicine tetracycline hydrochloride. The composite's antimicrobial activity was tested using zone inhibition opposed to gram-positive and gram-negative bacteria, and the results show that it has high antibacterial activity. As a result, the synthesized composite fiber has good properties for wound dressing and skin engineering uses [54].

Kahdim et al. prepared biocompatible scaffolds using PCL, chitosan (CS) and Nigella sativa (NS) seed extract and investigated their antibacterial activity against Escherichia coli and Staphylococcus aureus. The prepared PCL/CS/NS scaffold had better antibacterial properties, with an inhibition zone of 8.00 ± 0.22 mm for S. aureus and 7.4 ± 0.16 mm for E. coli compared to PCL and PCL/CS [55]. It was shown that the larger the diameter of the inhibition zone, the greater the antibacterial activity of the scaffold; thus, scaffolds containing PCL/CS/NS were more effective against S. aureus.

In a study by Ahmed et al., ε-PCL scaffolds were loaded with various amounts of silver-Fe_3O_4 nanoparticles. The silver nanoparticles in the nanocomposite acted as antimicrobial agents against E. coli and the healing process took place without any damage to the dermal and epidermal tissues of the skin [56].

Wang et al. prepared PCL electro-spun nanofiber membranes containing different concentrations of pomegranate peel extract (PPE). The diameter of the inhibition zone of PCL/10PPE against E. coli and S. aureus reaches 19.15 ± 0.76 and 22.81 ± 0.29, respectively. These superior antimicrobial activity results can be explained by the high levels of polyphenols in PPE, which inhibit microbial biofilm formation, thereby reducing their growth and proliferation [57].

Teodoro et al. prepared a low-cost, multifunctional therapeutic wound dressing by loading curcumin (CC) into PCL nanofibers. This PCL/CC dressing was successful in fulfilling various functions, such as controlled release of CC, colorimetric monitoring of wound conditions, and barrier formation against microorganisms. In addition, a study of the proposed wound dressing (PCL/CC) on mice showed a reduction of bacteria present in the wound [58].

Hui et al. synthesized PCL/PAA/PEI-CMC Janus membrane to be used as a wound dressing to prevent adhesion of external bacteria and promote wound healing. When this membrane was exposed to bacterial solution, a large number of bacteria adhered to the hydrophilic side of the membrane (PCL/PAA/PEI-CMC), while no bacteria were found on the hydrophobic PCL side. This result demonstrated that the Janus hemostatic membrane was able to resist the invasion of external bacteria and thus prevent wound infection [59].

2.3. PCL Blends/Composites for Drug Delivery

The micro- and nanofiber structures of PCL blends/composites have a high surface area/volume ratio and therefore have high drug loading and release potential. El Gohary and colleagues used Oil/Water emulsion solvent evaporation method to fabricate PCL/Fe_3O_4 microspheres with magnetic properties. This prepared magnetic PCL was effective and successful in the delivery of Lornoxicam to the knee joint [60].

The advancement of a PCL electro-spun composite coated with pectin/polyaniline (PANi) that was elucidated and had a use for drug delivery was described in the work of Hamzah et al. The SEM micrograph showed a powerful interaction between the bilayer structures and the interlinked pores of uniform fibers. The composition pectin(12%)/PANi(3%) was discovered as the maximized composition with a high tensile strength of 55.48 ± 0.65 MPa and a modulus strength of 63.30 ± 0.43 MPa. This combination of desirable mechanical properties will make the double-layer composite a dynamic and versatile scaffold for drug delivery [61].

Gizaw et al. produced microfibers at various blend ratios by adding acetylsalicylic acid (ASA) to blend fibers consisting of 15 wt% PCL and 4 wt% CS using an electrospinning method [62]. Drug release was studied in PBS buffer solution and 30% ASA was released up to 2 h. In ASA drug release, the amount of release increased as the amount of CS increased, which was attributed to the surface wettability property of CS.

Another investigation involved the development of solvent cast films containing different ratios of PCL:Poly(lactide-co-glycolide) (PLGA). Formulations with higher concentrations of PLGA and triethyl citrate as plasticizer showed a lower burst effect, while higher 5-Fluorouracil (5FU, an anticancer drug) loading (2%) resulted in an increased release rate [63].

2.4. PCL Blends/Composites for Other Applications

Other biomedical applications include fixation of broken bones in the form of plates, pins, screws and wires, as well as optical sensors and biosensors [64]. In addition to these biomedical applications, PCL blends have important uses in biodegradable packaging as described in the following two articles.

Zhang et al. presented novel, high-performance lignin-PCL-based polyurethane bioplastics. The PCL was added to the lignin as a biodegradable soft segment via a hexamethylene diisocyanate (HDI) bridge with long flexible aliphatic organic chains and high activity. Investigation was carried out into how the NCO/OH mole ratio, lignin content, and PCL molecular mass affected the characteristics of the resulting polyurethane plastics. It is crucial to note that the polyurethane film retained high tensile strength (19.35 MPa), elongation at break (188.36%), and tear strength (38.94 kN/m) when the lignin content reached 37.3%; additionally, it was remarkably stable at 340.8 °C and displayed exceptional solvent stability. An efficient method for enhancing lignin processability and creating sustainable bioplastic materials, like sealing compounds, biodegradable packaging films, and bio-adhesives, is the accomplished production of lignin-based polyurethane bioplastics [65].

According to Gorrasi et al., a new thermoplastic biodegradable compound (m-PCL-Pectin) was produced using a solvent-free method by altering natural pectin with m-PCL, a compound with pendants made of glycidyl methacrylate and maleic anhydride. Films were produced by processing the obtained material while it was still molten. The structural, thermal, mechanical, and barrier features to water vapor of pure pectin and modified PCL films were evaluated and compared. The suggested green method presents an excellent chance to produce fruit waste in order to obtain flexible and completely biodegradable polymers for packaging uses, as an intriguing replacement for conventional thermoplastics that are not biodegradable. According to analysis of mechanical properties, pectin's high rigidity and stiffness, as shown by stress at break and elongation at break point, severely restrict its use in the flexible packaging field. However, thanks to this approach, the elongation at break is significantly increased in the presence of PCL, which eliminates the limitation in pectin [66].

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