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تحضير النانو سيليلوز من بعض مخلفات النبات واستخدامها في إزالة الملوثات

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Chapter One

Introduction

1. General Introduction

Pollution is a problem that requires knowledge of how to get rid of it; this problem is becoming more serious because of the obvious role that man plays in exacerbating it [1]. One of its types is environmental pollution which includes soil pollution because of chemicals or acid rain [2]. As well as, this air pollution caused toxic volatile compounds, and pollution of groundwater because of organic and inorganic compounds which leaked in to the water.[3]. Pollution of groundwater and wastewater, it also comes from public institutions [4]. The problem of environmental pollution is increasing in developing countries and advanced industrially and especially the problem of wastewater pollution according to humanitarian and global organizations considered it a source of concern and from industries that increase pollution problem wastewater, are industries dye textile, leather, wood and plastic materials which use dyes to color their products many drinks of water are used, so it produces many colors in water of small amounts of dyes, which is very clear and undesirable [5]. The annual production of yarn dyes and textile is more than (10%) are discharged as liquid waste [6]. The term colorants refer to the substance capable of transmitting its color to the substrate [7] The removal of color from waste effluents becomes environmentally important because even a small quantity of dye in water can be toxic and highly visible [8] Concerted research efforts in the field of synthetic dyes and rapid industrialization of textile production resulted in the almost complete replacement of natural dyes by synthetic dyes on account of their easy availability in ready-to-apply form, the simple application process, consistency of shades, and better fastness properties [9] Therefore, the textile processing industry has imposed strict bans on certain synthetic dyes and auxiliaries which are posing serious challenges to sustainability issues. This has led to tremendous current excitement in the search for environmentally friendly products which can offer suitable alternatives/co-partners to these agents [10] One of the main sources of the severe polluting problem worldwide is the textile industry and its wastewaters containing dyes, 10 – 25% of the textile dyes are lost[11]. Are mainly classified into cationic, anionic, and non-ionic dyes [12]. Adsorption plays an important role in water and wastewater treatment [13]. Most of the adsorbents are easily available and low-cost but they have some disadvantages such as poor mechanical and heat resistance and relatively limited adsorption capacity for dyes [14]. The properties of magnetic adsorbents have opened a new field in engineering separation applications [15]. A large surface area and the abundance of adsorption sites are essential for the adsorption and removal of contaminants from wastewater [16]. Nanocellulose is considered as a new class of eco-material with many advantages, such as nanoscale dimension, renewability, high surface area, specific high strength and modulus, unique morphology, and good optical properties [17]. Nanoscience and Nanotechnology Have Piqued Researchers' Interest in Recent Decades Due to Their Dynamic Properties and Applications [18-21]. Nanotechnology (Or "Nanotech") Is Concerned with Atom and Molecular Manipulation. It Was Then Brought to A Definite Level, With One-Dimensional Sizes Ranging From 1 To 100 Nanometers [22–26]. The ability to observe and manipulate a single atom or molecule is a feature of both nanotechnology and nanoscience. Cellulose-derived nanomaterials are important in the field of nanotechnology. At the moment, researchers are exploring various strategies for creating materials on purpose .The advantages of using nanoscale materials include better light spectrum control, greater strength, and better chemical reactivity than their large-scale counterparts Nano cellulose (NC), one of today's hottest super materials, is widely utilized. Due to its light, transparency, and strong characteristics, it has many applications in the pharmaceutical, food, and electronics industries. Any naturally occurring cellulosic source material, like wood pulp, can be used to make NC because it contains "Nanofibers" tiny structures that resemble tiny needles. The systematic preparation strategy was developed using both top-down and bottom-up methods. It is made from plant material that has been purified, homogenized, and reduced into small pieces in order to remove non-homogenous compounds like lignin .The production of nanocellulose is entirely neutral [27]. Even though NC has a variety of physical and chemical characteristics, it makes salt water drinkable. The use of cellulose Nanofibre is becoming more popular. Furthermore, cellulose nanofibers can be reinforced more effectively than the macro- and microfiber feedstocks currently in use thanks to their higher aspect ratio. Cellulose is the major biodegradable polymer abundant on the earth. It is found in structural components of the cell wall of all green plants [28]. It is a polysaccharide compound and the homo polymer of glucose. A large number of glucose units combine to create a cellulose polymer molecule, which depends on their chain length and the average polymerization [29]. The construction of cellulose is (β 1→ 4) linkage [30]. It shows a very low conductivity and high resistivity of electricity. Based on solubility nature cellulose is classified into three groups. They are a, b and c. Among them, a is insoluble, b is precipitate in nature and c is completely soluble. [31]. Among the various organic nanoparticles, cellulose nanoparticles have encountered an enormous consideration for diverse causes. Nevertheless, cellulose has several substantial practical applications such as being renewable, biodegradable, environmentally friendly, low-priced, and possessing enormous mechanical strength [32]. Cellulose is the most abundant polymer and it is the main component of most plant biomass [33]. various methods can be used to obtained nanocellulose, such as acid hydrolysis, ultrasonic technique, and enzymatic hydrolysis [34,35,36]. The method that most widely used is acid hydrolysis [37].

1.2. Literature survey

Nanotechnology is currently widely employed and renewable due to its huge potential in a variety of development, research, and application domains. For the time being, Nano-cellulose has been used in several investigations since it is environmentally friendly. It has been used in many applications in the industry, medicine, agriculture, also pollutant removal and cosmetics.

(Alemdar and Sain,2008), Cellulose nanofibers were extracted from the agricultural residues, wheat straw and soy hulls, by a chemi-mechanical technique to examine their potential for use as reinforcement fibers in biocomposite applications. Chemical characterization of the wheat straw nanofibers confirmed that the cellulose content was increased from 43% to 84% by an applied alkali and acid treatment. FT-IR spectroscopic analysis of both fibers demonstrated that this chemical treatment also led to the partial removal of hemicelluloses and lignin from the structure of the fibers. XRD results revealed that this resulted in improved crystallinity of the fibers. After mechanical treatments of cryocrushing, disintegration and defibrillation, the thermal properties of the nanofibers were studied by the TGA technique and found to increase dramatically. The degradation temperature of both nanofiber types reached beyond 290 °C. This value is reasonably promising for the use of these nanofibers in reinforced polymer manufacturing [38].

(Reddy and Yang,2009), Natural cellulose fibers with cellulose content, strength, and elongation higher than that of milkweed floss and between that of cotton and linen have been obtained from the stems of common milkweed plants. Although milkweed floss is a unique natural cellulose fiber with low density, the short length and low elongation make milkweed floss unsuitable as a textile fiber. The possibility of using the stems of the milkweed plant as a source for natural cellulose fibers was explored in this research. Natural cellulose fibers extracted from milkweed stems have been characterized for their composition, structure, and properties. Fibers obtained from milkweed stems have about 75% cellulose, higher than the cellulose in milkweed floss but lower than that in cotton and linen. Milkweed stem fibers have low % crystallinity when compared with cotton and linen but the strength of the fibers is similar to cotton and elongation is higher than that of linen fibers. POLYM. ENG. SCI., 2009. © 2009 Society of Plastics Engineers [39].

(Svensson , 2012), in his thesis explores how to use the dry Nanoporous structure of cellulosic fibers in new types of composite materials . A large effort was also given on how to correctly characterize the structure of fibers where the wet structure has been preserved also in the dry state . Delignified wood fibers have an open fibrillar structure in their water-swollen state .This open fibrillar structure was preserved in the dry state by performing a liquid exchange procedure and the samples were thereafter carefully dried with Ar (g) .This open structure was also revealed using (FE-SEM) field emission scanning electron microscopy[40].

(Shokrollah , et al. 2014), showed the extraction of eosin dye from aqueous solution using a non-ionic surfactant. The enrichment of dye was determined by a spectrophotometric study. The effects of different operating parameters, e.g., salt, temperature,and concentrations of surfactant, pH , equilibration temperature , heating time and time, of centrifuge have been studied , and its absorbance was measured at 533 nm [41].

(Ibrahim, et al. 2015), Cellulose nanocrystals (CNCs) were obtained from native cotton fibers by sulphuric acid hydrolysis with a range of 30% to 60%, followed by sonication using ultrasonic technology. Nano cellulose has been characterized by transmission electron microscopy (TEM) scanning electron microscopy (SEM) and atomic force microscopy (AFM), X-ray diffraction (XRD), and Fourier transformed infrared (FTIR) spectra. TEM and SEM showed nanofiberes - like morphology for low acid concentration, while increasing the acid rate to 40% - 60% showed rod-like shape particles and spherical nanoparticles. Nanocellulose was quite different from that of unsonicated samples. X-ray diffraction data showed that the fibres had been transformed from cellulose (native) to nano cellulose crystal structure, which manifests significant conversion of cellulose. Nanocellulose exhibited identical FTIR spectra quite different from that of unsonicated samples. [42].

(Dossanios, et al. 2016), In recent years, several studies have been performed using nanocellulose as a component in polymeric nanocomposites. The interest in studying cellulose-based nanocomposite is due to the abundance, and renewable nature, and outstanding mechanical properties of this nanoparticle. However, obtaining nanocomposites based on nanocellulose, with optimal properties, requires good nanoparticle dispersion in the polymeric matrix. The chemical compatibility between nanofiller and polymer plays a major role in both the dispersion of particles in the matrix and the adhesion between these phases. The aim of this review is to present the fundamental concepts about nanocellulose, such as its structural aspects, production methods and current trends in classification, and the main aspects of cellulose-based nanocomposites, including the progress that has been reached in relation to their compatibilization, production, final properties and potential applications [43].

(Bekiroglu and Elmas ,2017),in their research showed recycling paper waste it's one of the best options for sustainable development and reducing waste. Because waste paper recycling supplies significant contributions to the sustainability of forestry resources, to energy saving efforts, to reduction of environmental pollution levels and to the effective utilization of raw materials. The economic contribution of waste paper recycling can be much greater if these wastes are collected at the source . Economic realization of this contribution can only be achieved through knowledge of the qualitative and quantitative properties of recycled waste paper [44].

(Widiarto, et al. 2017), Cassava peel is an agro-industrial waste that is available in huge quantities in Lampung Province of Indonesia. This work was conducted to evaluate the potential of cassava peel as a source of cellulose and nanocellulose. Cellulose was extracted from cassava peel by using different chemical treatments, and the nanocellulose was prepared by hydrolysis with the use of sulfuric acid. The best methods of cellulose extraction from cassava peels are using alkali treatment followed by a bleaching process. The cellulose yield from this methods was (17.8%) of dry base cassava peel, while the yield from nitric and sulfuric methods were about (10.78)% and (10.32%) of dry base cassava peel respectively. The hydrolysis was performed at the temperature of (50°C)for (2 h). The intermediate reaction product obtained after each stage of the treatments was characterized. Fourier transform infrared spectroscopy showed the removal of non-cellulosic constituent. X-ray Diffraction (XRD) analysis revealed that the crystallinity of cellulose increased after hydrolysis. Morphological investigation was performed using Scanning Electron Microscopy (SEM). The size of particle was confirmed by Particle Size Analyzer (PSA) and Transmission Electron Microscopy (TEM). [45].

(Khaleel, et al. 2018), This study aims to prepare the Nano-cellulose in a developed way, using an ultrasonic device. In this research, waste paper residues isolated from the other wastes were completely used. Usually, the initial residues of the waste paper industry will be deposited in the waste. This will cause pollution to the environment. In this way, we will eliminate one of the environmental pollution factors by producing new material from these residues, namely, cellulose Nano-particles. These substances have a high content of lingo cellulosic components that can be converted to the Nano cellulose structures. The acidic decomposition method by 50% sulfuric acid, and the ultrasonic device were used. After cooling and drying, the Nano-cellulose was obtained and the diagnosis was made by SEM, AFM, and FT-IR [46].

(Madureira, et al. 2018), indicated that Pineapple peel be a good source of cellulose for the production of cellulose nanocrystals . Peels from fresh-cut fruit was used as raw material . These residues were purified to remove pigments, lipids and hemicellulose, and a bleaching process for delignification was carried out for (4-6)h. All resulting products were characterised for their lignin, hemicellulose, cellulose and ash contents using standard techniques . The purified cellulose was subject to acid hydrolysis for nanocrystal extraction with two testing times, (30 and 60) min. The time of extraction did not affect the nanocrystals chemical and physical properties. The use of(6) h of bleaching treatment during purification was shown to be more effective than(4) h [47].

(Hossain, et al. 2018), in their work explained the derivation of nanocellulose from an alternative option which is rice husks . The processed rice husks was refined by chemical and mechanical treatments . Nanocellulose was subsequently derived from the refined rice husk through acid hydrolysis followed by centrifugation and ultrasonic treatment. Scanning Electron Microscopy ensured the nanoscale diameter while Fourier transformed infrared Spectroscopy confirmed the removal of noncellulosic materials. It is therefore proposed that the native rice husk can also be utilized for manufacturing nanocellulose reducing its adverse environmental impacts [48].

(Chen, et al. 2019), In the present study, we attempted revalorization of pear (Pyrus pyrifolia L.) peel residue into high value-added nanomaterials. A green and facile one-pot isolation procedure was designed to simplify the isolation process of nanocellulose directly from pear peel residue. The one-pot approach employed in this work is interesting as the reaction involved less harmful chemicals usage and non-multiple steps. The reaction was carried out by adding hydrogen peroxide as an oxidant and chromium (III) nitrate as catalyst in the acidic medium under mild process conditions. FTIR spectroscopy proved that the pear peel derived nanocellulose was purely cellulose phases without the presence of non-cellulosic layer. XRD study indicated that the isolated nanocellulose possessed of cellulose I polymorph with high crystallinity index of 85.7%. FESEM analysis clearly revealed that the considerable size reduction during one-pot process. Remarkably, TEM analysis revealed that the isolated nanocellulose consisted of network-liked nature and spherical shaped morphologies with high aspect ratio of 24.6. TGA showed nanocellulose has lower thermal stability compared to pear peel residue. This study provided a cost-effective method and straightforward one-pot process for fabrication of nanocellulose from pear peel residue. This is the first investigation on the nanocellulose extraction from pear fruit. [49].

(Rong, et al. 2020), Iron nanoparticles (KP-FeNPs) were successfully synthesized using Korla fragrant pear (Pyrus sinkiangensis Yu) peel extracts through a green synthetic method. The KP-FeNPs were characterized by TEM, SEM, XPS, XRD, and FTIR, and subsequently used to remove Cr(VI) from aqueous solutions. The

KP-FeNPs were irregularly-shaped and ranged (20 – 90) nm in size. Iron in the KP-FeNPs was mainly present as zero-valent iron (Fe0), divalent iron (Fe(II)), and trivalent iron (Fe(III)) oxides. These were coated with polyphenols, flavonoids, and other natural organic compounds from the extracts, which acted as stabilizing and capping agents. When the temperature increased and when the initial Cr(VI) concentration decreased, the removal efficiency of Cr(VI) increased. The experimental adsorption data were fit well by both a Langmuir isotherm model and a pseudo-second-order kinetic model. The maximum Cr(VI) adsorption capacity (qm) of KP-FeNPs was(46.62 mg/g) at (55 °C) and a pH of 5.0. The KP-FeNPs removed 99.1% of Cr(VI) within 120 min from an aqueous solution containing 10 mg/L at (55 °C) and pH 5.0. This was much larger than that removed by the peel extracts (2.05%) or by Fe(II) (13.9%). The influence of five anions (NO^{-3}, Cl^{-}, $SO4^{-2}$, $CO3^{-2}$, and $PO4^{-3}$) on Cr(VI) removal and their removal effects in real water samples were also studied. [50].

(Tavker, et al. 2021), Nano-fibrillated cellulose (NFC) was extracted by a chemical method involving alkali and acid hydrolysis. The characterisation of the citrus sinensis fruit peel bran and nano-fibrillated cellulose was performed by XRD, FTIR, TEM, and FESEM. XRD confirmed the phase of NFC which showed monoclinic crystal with spherical to rod shape morphology with a size of 44–50 nm. The crystallinity index of treated NFC increased from 39% to 75%. FTIR showed the removal of lignin and hemicellulose from waste peels due to the alkaline treatment. Silver nanoparticles were also synthesised by utilizing extract of citrus sinensis skins as a reducing agent. Pharmaceutical effluent samples from an industrial area were tested by Atomic Absorption Spectrometry. Out of the four metals obtained, cadmium and chromium were remediated by silver nanoparticles with nano-fibrillated cellulose via simulated method in 100 mg/L metal-salt concentrations over a time period of 160 min. The highest removal efficiency was found for cadmium, i.e., 83%, by using silver and NFC together as adsorbents. The second highest was for chromium, i.e., 47%, but by using only NFC. The Langmuir and Freundlich isotherms were well fitted for the sorption of Cd (II) and Cr (II) with suitable high R2 values during kinetic simulation. Thus, the isolation of NFC and synthesis of silver nanoparticles proved efficient for heavy metal sorption by the reuse of waste skins. [51].

(Ariaeenejad, et al .2022), In this study, the synthesis of nanocellulose (NC) from an agro-waste of quinoa husks (QS) was reported for the first time. The NC nano-carrier was utilized for immobilization of a model laccase enzyme (PersiLac1) providing an innovative, green, and practical nano-biocatalyst for efficient removal of two different model dyes (malachite green (MG) and congo red (CR)) from water. This nano-biocatalyst developed a synergistic adsorption-degradation approach leading the dye molecules easily gathered near the nano-carrier by adsorption and then degraded effectively by the enzyme. Upon enzyme immobilization, the dye removals (%) were remarkably improved for both 150 mg/L of dyes (from 54% and 12%, for MG and CR, respectively, in case of the pristine NCs, to 98% and 60% for the immobilized enzyme). The immobilized PersiLac1 could decolorize the concentrated dye solutions and showed superior reusability (up to 83% dye removal after 18th runs for MG) and remarkable performance from complex real textile effluents [52].

1.3. The Aim of the study

This study aims at:

Preparation of Nanocellulose from cotton lint and pear peels instead of throwing it as waste and causing damage to the environment. Comparison between the efficiency of the product of Nanocellulose prepared from cotton lint and NC prepared from pear peels through the characterization of both types of NC by using techniques for characterization of Nano cellulose (Field emission scanning electron microscopy (FESEM), Atomic Force Microscope, X-ray diffraction (XRD), and Fourier Transform Infrared spectroscopy). Applying Murexide dye from the aqueous solution to the surface of both types of extracted Nanocellulose from cotton lint and pear peels for industrial waste. Utilizing agricultural waste recycling for practical reasons, particularly chemical adsorption.