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Emerging applications of chitosan: from biology to environment

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ABSTRACT
Chitosan one of the polysaccharide family own unique hydrogen bonding dedicates it to many applications. Many researchers reported the biological applications of chitosan according to its biodegradable nature. Many research papers are interested in the production of chitosan and its various applications in different fields. Chitosan is a potential biopolymer in food processing applications, drug delivery systems formulations, and industrial and energy production processes. The application of chitosan in the field of aquatic environment is as important as biological field as it is so called green method for safe environmental protection. The remediation of some harmful materials including pharmaceutical residues from wastewater is new trends whereas chitosan and its derivatives are dedicated to solve many problems in that field. The present review gave some introduction to some problem in the aquatic environment then it gives some remarks on the possible applications of chitosan in this field. The present review will cover the following points: some applications of chitosan, importance of environmental issues, the occurrence of medical residues in the environment, pharmaceuticals and personal care products (PPCPs), a common mechanism for removal of PPCPs, PPCPs removal following cost effective adsorption route, role of chitosan and its derivatives, role of molecular modeling, recent developments and conclusion.
Keywords: *Biomaterials, biopolymers, chitosan, chitosan derivatives, molecular modeling, biological applications, environmental applications.*

1. SOME APPLICATIONS OF CHITOSAN

(Many articles are found concerned with chitosan and its characteristics. Degree of deacetylation (DD), molecular weight and viscosity are the most significant parameters affecting chitosan features. Degree of deacetylation can be determined using various methods. Spectroscopic methods are the most commonly used ones. The impact of the utilized method in determining the degree of deacetylation (DD) of chitosan is investigated [1]. Hydrogen bromide titrimetry (HBr titrimetry), infrared spectroscopy (IR spectroscopy), and first derivative UV-spectrophotometry (FDUV-spectrophotometry) analytical methods are utilized in the determination and comparison processes. Three different chitosan samples were employed for the analysis processes. KBr disc and thin film formulations were used for the IR spectroscopy analysis. Results of DD obtained by HBr titrimtey method was lower than both obtained from IR spectroscopy with films and FDUV spectrophotometry. However, it was higher than those resulted from KBr discs except for Chit-S2. Moreover, the results obtained using IR spectroscopy differed according to the used baseline. The article concluded that the calculated DD values are dependent on the used analytical procedures and the method used in its quantification should be mentioned. The DD of chitosan using different methods is determined [2]; FTIR spectroscopy, potentiometric titration and CHN analyzer were utilized in order to study their impact on the release rate of oils. Chitosan and chitosan/gelatin complex microspheres were synthesized. The chitosan deacetylation process was obtained by alkali treatment for different time intervals. Results the higher the alkali treatment is, the higher the DD will be. Hence lowering the release rate of encapsulated oil as well as increasing swelling degrees due to the increment of the number of amine groups. However, it lowered the smoothness of the spheres. High crosslinking degree decreased the release rate as well as swelling. Both chitin and chitosan biopolymers are characterized using ultraviolet and mid-infrared radiations [3]. Recording the absorption spectra in these conditions enabled them from quantifying the DD in their structures. The article defined the DD as the ratio of the units of glucosamine to their sum with the N–acetyl–glucosamine ones. In addition, the research showed that all of the molecular mass, DD and the crystallinity are the main structural parameters that affect the chitosan features such as its solubility, mechanical resistance as well as its degradability. Researches on the possibility of its development as a natural antimicrobial agent have been increased during the last decades. Chitosan can be applied to extend the storage life of different categories of food materials. It can be used as a natural antimicrobial material rather than synthetic preservatives that have well known hazardous effects. Both chitosan and chitosan derivatives were utilized to study the effect of their molecular weight, DD, solution pH on their antibacterial activity against E-coli. Chitosan, N,O-carboxymethylated chitosan and O-carboxy methylated chitosan were synthesized [4]. Their results indicated that the antibacterial activities increased in the order of N,O-carboxymethylated chitosan, chitosan, and O-carboxymethylated chitosan. Furthermore, the antibacterial activity of chitosan seems to be caused mainly by the inhibition of the transcription from DNA. The antibacterial activity was increased with the MW varying from 5 kDa to 91.6 kDa and decreased with MW varying from 91.6 kDa to 1080 kDa. Also, it increased by increasing DD or solution concentration. The results showed that the 6.3 pH is the optimum one for antibacterial activity. Biopolymer composites of chitosan were prepared with both polyvinyl alcohol (PVA) and bacterial cellulose [5]. They were formulated in the form of films. The research aimed to study the characteristics of the composite films in order to evaluate their usage in food packaging processes. PVA-chitosan films were found to be not water resistant. In addition, FTIR analyses of the formulated samples illustrated strong interactions between chitosan and both PVA as well as bacterial cellulose. Moreover, the analysis proposed that these composite films could be utilized as antimicrobial food packaging materials. The antimicrobial activity of four different chitosan films with viscosities 10, 40, 100 and 200 mPa.s was investigated against *Listeria monocytogenes, Escherichia coli 0157:H7 and Samonella typhimurium* [6]. Chitosan films of 100mPa.s showed an antimicrobial effect only against a certain concentration of *L. monocytogenes* while other viscosities showed an antilisterial effect against all others. Those prepared with 10mPa.s and 40mPa.s showed an inhibitory effect against *E. coli* 0157:H7 and *S. typhimurium* of a certain concentration. Other chitosan films did not show any effect regardless of bacterial level. They supposed that chitosan films have high antimicrobial activity especially against *L. monocytogenes* rather than *S. typhimurium and E. Coli O157:H7.* Furthermore, chitosan has been used in food industry and manufacturing. Being water-insoluble, biocompatible and biodegradable gave it the priority in many food applications. Thus, chitosan as well as chitin have been used to extend lifespan of different fresh fruits and vegetables and frozen and fabricated foods. Chitosan with different concentrations (1.0 and 1.5 % w/v) were used as a coating material for bell pepper and cucumber fruits [7]. The weight loss, respiration and quality of the fruits were monitored to study the effect of chitosan coating on their storability at 13^{o}C and 20^{o}C and relative humidity 85%. Results showed that chitosan coating had a great ability to reduce the weight loss in both fruits at both temperatures. This ability increased by increasing its concentration from 1.0 % w/v to 1.5 % w/v. Also, chitosan coating reduced the respiration rate, loss of color; wilting and fungal infection. Chitosan and crosslinked chitosan films were prepared [8]. They were investigated as food packaging materials. Barrier characteristics for water vapor, oxygen transmission rates and grease resistance were studied. Their mechanical properties such as burst strength, tear resistance and tensile strength were also calculated. Results demonstrated that the prepared films have moderate water vapor transmission properties. They also had low oxygen permeability. The mechanical properties of the films were low compared with commercial plastics. The research results ensured that chitosan films could be utilized as food packaging material where they proved efficiency in extending the lifespan of fresh food. Chitosan biopolymer was utilized as coating films to extend the shelf-life of fresh fillets of Atlantic cod (*Gadus morhua*) and herring (*Clupea harengus*) [9]. The aim was to preserve them over twelve days storage refrigerated temperature (4 ± 1 °C). Different chitosan molecular weights with various viscosities were investigated. Results showed that usage of chitosan coats reduced the moisture loss up to 40% for the cod samples treated with 360 cP chitosan film after 10 days. The efficiency of chitosan samples of viscosities 57 and 360 cP was higher than that of 14 cP viscosity one. In general, usage chitosan as coating films enhance the properties of the tested samples and hence extend their shelf-life span and improved their quality. Chitosan was incorporated in unpasteurized orange juice [10]. Its addition was evaluated testing the juice quality and using nutritional markers. The analyses showed that increasing chitosan concentration extended the quality of the orange juice, reducing enzymatic and non-enzymatic browning and controlling the spoilage during the storage time. However, concentrations greater than 1 g/L produced a significant reduction in the concentrations of ascorbic acid and carotenoids. These results recommend the usage of chitosan at concentrations up to 1 g/L to extend quality and preserve ascorbic acid and carotenoids during storage time of fresh orange juice. Many research papers focus on utilizing biopolymers as drug delivery carriers in order to control their release. Using natural polymers have been proved a significant impact on the control process of the different drugs. They showed better performance compared to those in the free form. In addition, biopolymers provide much economic strategy for controlling release rates of drugs. Controlled release drug delivery system of chitosan was prepared [11]. The formulated system was of two layers; inner core layer of hydrophilic chitosan and outer shell one of hydrophobic cellulose. The prepared particles were of size smaller than 70μm. The formulated particles enclosed two types of drug and protein named sodium diclofenac (SD) and fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA). The encapsulation efficiency of SD was high. Results showed that the release rate behavior can be adjusted by varying the core properties such as molecular weight and core/coat ratio or the coating polymer. Low pH media provided the microparticles with stability and confirmed that they are proper for oral delivery. Both chitosan and its derivatives were formulated, such as N-trimethyl chitosan (TMC) and mono-N-carboxymethyl chitosan (MCC), to be used as drug delivery systems [12]. They were utilized in order to enhance the immune response of mucosal vaccines and/or antigens. Results showed that the formulated nanoparticles were of high encapsulation efficiency (>90% m/m), particle size of 40-400nm and negative surface charge for MCC while a positive one for TMC and chitosan. In addition, their cytotoxicity properties were studied on Chinese hamster ovary (CHO-K1) cell lines. Results illustrated that cell viability was in the order of MCC, chitosan and TMC. The research proposed that the formulated nanoparticles can be used as promising adjuvant/delivery systems for mucosal immunization. The release rate of acidic diclofenac sodium (SD) in various formulations was studied [13]. They compared the release rate of the prepared samples with the free pure drug dissolution. Its releasing processes were carried out in phosphate buffer (pH 6.8). It was enclosed in mesoporous silica and two spherical silica. In addition, SD was encapsulated in composites of silica with chitosan. It was used in both protonated and deprotonated forms. The structure of diclofenac became more amorphous after encapsulated which help in increasing its dissolution rate. Results showed that the release rate of diclofenac was dependent on the porous structure of the carrier and increased with increasing pore diameter. The release rate was prolonged when using hydrophobic silica. Protonating chitosan reduced the release rate of diclofenac significantly from 30mg/h to 1.5mg/h. In addition to the common applications of chitosan, various papers interest in enhancing its features in order to be used in other fields. The chemical and physical stability of chitosan films through the addition of silica and polyethylene glycol (PEG) polymer were developed [14]. Results showed that as the amount of the added silica increased, both of the tensile strength as well as the elongation percentage decreased. Moreover, by adding PEG, the tensile strength would diminish, however the percentage of elongation increased. Increasing the silica amount reduced the hydrophilicity of the prepared films while it increased by adding PEG. Silica and PEG addition did not affect considerably the morphology of the modified films. FTIR results ensured that there is a physical interaction among active sites and no chemical one occurred since no change in the peaks of functional groups took place. Different membranes are prepared of chitosan-grafted-polyvinyl alcohol/polyvinyl alcohol (CS-g-PVA/PVA), chitosan (CS), polyvinyl alcohol (PVA) and chitosan/polyvinyl alcohol (CS/PVA) composites [15]. Their characteristics were investigated and compared with Nafion 117 regarding their water and methanol transport properties, mechanical properties and electrical conductivity. However better properties Nafion 117 had according to its mechanical properties and proton conductivity, its high cost and high methanol uptake which could lower proton conductivity dramatically makes CS-g-PVA/PVA membrane better choice. Results proposed CS-g-PVA/PVA as a potential alternative material to be used as an electrolyte membrane in a direct methanol fuel cells. Modified chitosan membrane with silica nanoparticles was prepared [16]. Nano silica was mixed with chitosan solution to obtain nanosilica-chitosan in order to be used as a polyelectrolyte membrane (PEM). They functionalized chitosan in PEM applications to replace Nafion. The article aimed to overcome Nafion shortcomings. It has high methanol permeability that degrades the performance of fuel cells. Results showed that chitosan modification with nanosilica at 3% ratio produces membrane with better characteristics in terms of membrane selectivity, water swelling, proton conductivity and methanol permeability. Water swelling and proton conductivity increased with increasing nanosilica ratio. On the other hand, methanol permeability decreased with increasing of nanosilica composition. Chitosan was modified with silica nanoparticles and doped with Ru $(bpy)_3^{2+}$ (bpy = 2,2'-bipyridyl) as reference dye and pH sensitive fluorescein isothiocyanate (FITC) as pH indicator [17]. Such novel structures were used as fluorescent nano sensor for measurement of surface pH of paper arts. The formulated nano sensor showed linear behavior in the pH range of 5.5 to 8.0. Results illustrated that by using a flexible linker between the prepared nanocomposites and molecular probe, the resulting nano sensor showed an excellent ability to detect the surface component. Moreover, having small size and good ability on signal amplification for many dye-doped nanocomposites, this may make it a good nano probe to image the components on the surface of the culture heritage with both high sensitivity and spatial resolution.

2. IMPORTANCE OF ENVIRONMENTAL ISSUES

Over the last decades, environmental issues received the greatest concern in research compared with other fields [18]. Water and energy have become the most important topics in the research community during the last thirty years. Having new strategies provide renewable sources of energy instead of non-renewable ones as well as ones enable us from purifying water from the various pollutants so that we can reuse it again in various purposes are now the leading trend of research. The industrial revolution occur in the last centuries enable humanity from having advanced life styles as well as improve greatly the life on different levels; health, communication, food industry, technology, transportation and many other sides. On the other hand, such an industrial revolution has a great influence on increasing the percentage of the environmental pollution. The increment in the pollution percentage threatens the life on the earth. It becomes the main reason of the appearance of new diseases that we ever have heard, in addition to many other environmental problems [19]. The emerging of various industrial products in the different forms of water; drinking, surface and ground water, treated and untreated sewage effluents, sediments and sludge, affects the life of plants, animals as well as human. Water pollutants can be classified into two main categories; organic and inorganic pollutants. Inorganic pollutants are usually defined as chemicals that are of mineral origin and not produced by living organisms. Such pollutants have many examples like heavy metals and their salts, inorganic fertilizers produced from agricultural activities (nitrates and phosphates) and sulphides (Pyrite). They were extensively discovered in water and many research articles focused on their investigation. Hundreds of research papers focused on strategies of their removal from water. The other class of pollutants is the organic waste. They are often defined as chemicals of organic origin and produced by livings. They are a large group of chemicals that recently discovered in the water. Thus, the latest researches have concentrated on finding organic pollutants, determining their concentrations and sorting them in the well-known categories. Among the various branches of organic pollutants organic solvents including acetone, toluene, benzene and xylene, polycyclic aromatic hydrocarbons (PAHs), organo-metalic compounds including organo-arsenicals and organo-mercurials and finally pharmaceuticals and personal care products (PPCPs) [20].

3. OCCURRENCE OF MEDICAL RESIDUES IN THE ENVIRONMENT

Pharmaceuticals and personal care products, as mentioned, are one of the most important and largest groups of organic products. They are daily consumed with huge quantities all over the world [21]. The technology involved in their manufacturing has become highly advanced. They include many goods that are used in various fields. They include human medicines, veterinary medicines, cosmetic products and agricultural products [22]. Medicines are also a wide class of PPCPs. They can be classified into many categories such as antibiotics, antihypertensive (beta blockers) drugs, blood lipid regulators and nonsteroidal anti-inflammatory drugs (NSAIDs) [23]. Antibiotics are one of the famous used drugs worldwide for their effects against bacterial infection. Their mode of action usually depends on the inhibition of enzymes involved in cell wall biosynthesis, metabolism of nucleic acid and repair, or protein synthesis. Antihypertensive drugs are used for their effective action against high pressure circumstances. Some antihypertensive drugs work to depress heartbeat rate by blocking the effect of sympathetic nerves on the heart. Calcium-channel blockers also reduce cardiac output by decreasing heart rate and contractility. Blood lipid regulators are often used for getting rid of extra lipids in body. They work to prevent the synthesis of harmful cholesterol that is the main cause of atherosclerosis. Finally, nonsteroidal anti-inflammatory drugs are the second consumed drugs after antibiotics all over the world. NSAIDs have been used worldwide with very huge quantities. Moreover, NSAIDs are usually used without any prescriptions all over the world, thus they often called "over-the-count" drugs or OTC drugs. NSAIDs have many useful effects on the body; they have analgesic and pain relief effects, antipyretic and fever reducing effects and anti-inflammatory and swelling reduction effects. NSAIDs are usually chemically classified into many categories such as propionic acid derivatives, acetic acid derivatives and enolic acid derivatives [24]. The propionic acid derivatives include Ibuprofen (IBP), ketoprofen and Fenoprofen compounds. The acetic acid derivatives include Diclofenac, Etodolac and Sulindac compounds. The enolic acid derivatives class includes Piroxicam, Meloxicam and Tenoxicam compounds. Ibuprofen is one of the common examples of NSAIDs. Intense usage of PPCPs lead to their continuous release into the environment [25]. Nowadays, NSAIDs and especially IBP becomes one of the serious pollutants that emerging in the different types of water; drinking water, surface water, rivers, lakes and sewage effluents [26]. Thus, it becomes vital to find a strategy for its removal from our water. Being synthetic and complex, like all the members of PPCPs class, makes it difficult to be treated with traditional methods or through sewage treatment plants (STPs).

4. PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS)

Emerging of pharmaceuticals and personal care products (PPCPs), medications and personal care products (PCPs) becomes one of the hot spots in the environmental sciences. Studies have been attracted to investigate their occurrence, fate, harms on human, animals, plants and the whole ecosystem and strategies of their removal [27]. They were detected with concentrations up to several μg/L [28]. Their hazards are incompletely understood yet. Getting pure water from different pollutants especially PPCPs has become one of the vital tasks for many research papers. Thus, an increasing number of research paper have a great passion to discover their behavior. They focused on detecting the presence of PPCPs in the different types of water. The presence of about thirty two medicines in the German municipal sewage treatment plant (STP) discharges, river and stream waters was investigated [29]. The detected medications belonged to various classes; lipid regulators drugs, antiphlogistics, psychiatric medicines, antiepileptic drugs, beta blockers and β_2-sympathomimetics, in addition to five metabolites. Some of them were of concentrations up to 6.3μg/L. Acidic, neutral as well as basic medicines were detected. Acidic drugs such as ibuprofen, diclofenac, bezafibrate, phenazone and metabolites of clofibric acid, fenofibric acid and salicylic acid. Neutral and weak basic drugs such as metoprolol, propranolol and carbamazepine medicines were found. They were mostly found in rivers and streams in the ng/L concentrations. The presence of PPCPs was investigated in the urban municipal sewage water of Berlin, Germany [30]. Many observation studies for the waters of Berlin were carried out from 1996 to 2000. PPCPs were detected in persist forms. Their concentrations were in the range of μg/L. Ibuprofen, diclofenac, carbamazepine, propyphenazone, clofibric acid and primidone were detected. Their individual concentrations reached to 7.3μg/L in specimens gathered from groundwater aquifers close to polluted water. They were found in both influent and effluent sewage treatment plants (STPs). In addition, they were monitored in rivers, canals and lakes. Presence of polar PPCPs were a serious sign of the pollution of the surface and ground waters since they are persistence and are not eliminated by the STPs. A new method was developed to measure the concentrations of nine PPCPs named ibuprofen, clofibric acid, naproxen, bisphenol A, estrone, chlorophene, 17β-estradiol, fluoxetine and triclosan [31]. The Water samples were taken from two surface water streams; a first one from a sewage treatment plant (STP) effluent and various phases of a drinking water treatment plant in Louisiana, USA. The second one was from a surface water stream, a drinking water treatment plant and a pilot plant in Ontario, Canada. Only three of the nine investigated drugs were detected; naproxen, clofibric acid and triclosan. Naproxen was found with concentrations of 81-106ng/L and 22-107ng/L in Louisiana STP effluent and Louisiana and Ontario surface waters, respectively. Triclosan was detected with concentrations of 10–21 ng/L in Louisiana STP effluent. Clofibric acid was found with concentration of 103ng/L in the three surface waters sampled in Detroit River water while not detected in Mississippi River or Lake Pontchartrain waters. The presence of PPCPs was investigated in the aquatic environment of China [32]. The research ensured that the sewage treatment plants are the main source of PPCPs. Its investigations ascertained that veterinary livestock are another source of PPCPs. Both of antibiotics and hormones were found to be the most frequently detected PPCPs in water. Their maximum concentrations reached to about several μg/L. The detected concentrations of hormones were less than those of antibiotics. Ibuprofen was among the highest frequently detected species and the highest concentrations with caffeine, diclofenac and carbamazepine.

5. COMMON MECHANISM FOR REMOVAL OF PPCPS

Many strategies and trials were conducted to remove PPCPs but each one has its own problem. Finding an effective, feasible and low cost processing method is now a great challenge in the water treatment field. Many research papers ascertained that conventional wastewater treatment plants are inefficient in removing PPCPs. This can be attributed to the synthetic nature of PPCPs. In addition, STPs are mainly designed for removing organic natural pollutants where they depend mainly on biodegradation processes using living microorganisms. Therefore, STPs become one of the potential sources of PPCPs in water.

Hence, they need further advanced methods in purifying water. The presence of PPCPs was investigated in Tone River, Japan [33]. It is characterized by its importance where it is not only for farming but also utilized as a source of drinking water. Seventy PPCPs were detected in the river. Water samples were gathered from surface water in the river, its tributaries, and effluents from sewage treatment plants (STPs) in two days of January and October 2006. The most frequently detected PPCPs were sulpiride, bezafibrate, crotamiton, caffeine, clarithromycin, and carbamazepine. The paper concluded that the presence of PPCPs in the Tone River suggested the necessity of constructing sewage systems. The occurrence of PPCPs is studied in drinking water of southern China [34]. Nearly fifteen ones were detected with concentrations 0-36ng/L in the water source. Eleven PPCPs were detected even in treated water with conventional methods with a concentration of 0-20ng/L as well as nine ones were detected in treated water with advanced treatment processes with a concentration of 0-3ng/L. The article ascertained that the state of conventional wastewater treatment methods were inefficient in purifying water. They reduced the PPCPs types by only 30% and their concentrations by more than 90%. While advanced treatment methods reduced the PPCPs types by 50% and the concentrations by 90%. Advanced processes showed an efficient behavior toward PPCPs. Both of adsorption and biodegradation processes are proposed to be promising for removing PPCPs. The occurrence of PPCPs was monitored in the Great Lakes in Michigan, USA [35]. It was proven that they are not regulated in either influent or effluent. PPCPs were detected in both of them. They tried to detect their concentration and corresponding hazards in a wastewater effluent at different distances from the Great Lakes. The concentrations of the detected PPCPs were in the range of ng/L range at about 3.2 km from the Lakes' shore. About 54 PPCPs and EDCs were found on 6 various dates around a two year time interval in the surface and sediment specimens. In addition, nearly 32 PPCPs were detected in Lake Michigan. Sulfamethoxazole, metformin, triclosan and caffeine were the most commonly found PPCPs there. The article ensured that the great dilution occur for the PPCPs is not enough for eliminating their harmful effects and hazards are much higher than expected. The presence of eight acidic medications in South Africa was investigated [36]. Waste and surface water are studied, and sediments from the Msunduzi River in the region of KwaZulu-Natal, South Africa. Four antipyretics, 3 antibiotics, and 1 lipid regulator compounds were investigated. Concentration levels of 1.16 ng/L and 29.1 ng/L were detected in water and 0.58 ng/g and 14.5 ng/g in sediment. Aspirin was the most abundant medication noticed with a concentration of 118 ± 0.82 mg/L in the influent of wastewater. Similarly, nalidixic acid was the most detected antibiotic with levels range from 25.2 to 29.9 mg/L in wastewater while bezafibrate was the least noticed one. The paper concluded that the wastewater treatment processes could not significantly lower the concentration of contaminants and serves as a surface water and sediment source. Due to the inefficiency of STPs in removing PPCPs, several methods were investigated in order to remove them from aqueous solutions as well as wastewater. Membrane filtration as well as photocatalytic degradation mechanisms are the major methods used in wastewater treatment. They are reviewed to be more efficient in eliminating PPCPs. It was found that the water source of Istanbul was spiked with three PPCPs named carbamazepine (CBZ), diclofenac (DIC) and ibuprofen (IBP) [37]. The performance of a nanofiltration membrane for removing the previously mentioned PhACs after effluent from a drinking water treatment plant was studied. Results showed that the rejection of neutral CBZ was 31-39% while that of ionic DIC and IBP was 55-61%. The high rejection amount of both DIC and IBP was attributed to their low solubility, high log Kow (octanol-water partition coefficient) values, low total dipole moment and their negative charges. The ability of heterogeneous photocatalytic degradation using titania (TiO_2) on mineralizing members of NSAIDs is investigated [38]. The used ones were ibuprofen, naproxen (NPX) and diclofenac. Xe-lamp reactor was used in performing the experiment. Several factors that supposed to affect the degradation process were studied such as catalyst quantity, dissolved oxygen concentration and temperature. The ecotoxicity of the produced metabolites was assessed using Vibro fischery species. 1000mg/L of TiO_2 was the optimum load for degrading IBP while only 100mg/L was enough for maximum degradation of both NPX and DIC. Temperature variation had no impact on the degradation rate of both IBP and DIC. Hydroxide ions were the most important produced metabolites of IBP. The produced hydroxyl metabolites led to inhibition of the studied Vibro fischery species by increasing the irradiation dose. The influence of sonolysis, photocatalysis and sonophotocatalysis methods for the removal and degradation of ibuprofen is studied [39]. The degradation processes were carried out in the presence of homogeneous (Fe^{3+}) and heterogeneous TiO_2 photocatalysts. The resultant intermediate species were identified. Mono and dihydroxylated intermediates of IBP were detected. Sonophotocatalysis was the most effective in its removing relative to the two other methods; sonolysis and photocatalysis. Photocatalytic oxidation method was utilized in removing ibuprofen [40]. Titania catalyst P25 was used. Ibuprofen had been mineralized rapidly upon treated with titania. Treatment of ibuprofen with titania photocatalyst resulted in the production of less toxic intermediate substances. Many factors affecting the photocatalytic process had been studied, such as catalyst and ibuprofen concentrations and the catalyst/ibuprofen ratio. The formed intermediates were suggested to cause poisoning for the catalyst and reduce its efficacy. Photodegradation of both carbamazepine and ibuprofen in aqueous solutions is studied [41]. The process was performed with the aid of TiO_2 and zinc oxide under the irradiation of UV or visible light. Factors affecting the photodegradation processes were investigated such as the catalyst type, the catalyst dose and the drug initial concentration. Isopropanol (HO• scavenger) was used in order to determine the nature of the photodegradation process. Results showed that photocatalytic degradation mechanism is the most predominant under visible light irradiation. The photocatalytic degradation of IBP was higher than that of CBZ. The photocatalytic behavior of TiO_2 was found to be higher than that of ZnO. Isopropanol addition had a significant impact on inhibiting the degradation rate of CBZ indicating it depends mainly on the production of HO•

free radicals in CBZ degradation. However it had no influence on IBP degradation indicating the predominance of electron/hole mechanism. The removal of ibuprofen was studied by TiO2 photocatalyst under the irradiation of UV light produced from both artificial source and solar source in a heterogeneous photocatalysis process [42]. Different concentrations range from 20 to 100mg/L of titania were investigated against ibuprofen solution of concentration 1 mg/L. Tracking the resultant intermediate species from the photocatalysis process was performed in a bioassay process. Both D. similis and the green algae R. subcapitata were utilized. Ibuprofen removal reached about 92% after only one hour. The highest removal percentage was obtained by 1g/L of titania and using the artificial UV rays. However the ibuprofen was not completely mineralized. The degradation of ibuprofen resulted in more toxic species that led to growth inhibition of both used D. similis and R. subcapitata by 30% and 40%, respectively.

Although nonconventional methods such as advanced oxidation processes are efficient in purifying water from various types of pollutants, they have numerous limitations. They are expensive, not applicable on large commercial scales and also may produce more toxic species than the parent compounds.

6. PPCPS REMOVAL FOLLOWING COST EFFECTIVE ADSORPTION ROUTE

Adsorption mechanism is now one of the most intensively used strategies in removing different waste materials. It is always used in removing heavy metals from aqueous solutions. Various materials are successfully used as adsorbent materials like activated carbon, charcoal, zeolites etc. Recently, natural polymers such as chitosan and other low processing cost adsorbent materials are reported in wastewater treatment and removing of PPCPs. Many research papers were published to illustrate the chitosan and other natural polymers utilization in removing various pollutants. In addition, the adsorption method has become one of the most feasible methods in pollutants removal. Many research papers focus on the usage of chitosan and its derivatives in the removal of various waste substances through an adsorption mechanism. They are tested for removing metal ions, inorganic wastes, organic wastes and pollutants of the pharmaceutical source. In addition, biopolymers provide a much more economic strategy for removing the various complex pollutants. One of the chitosan derivatives named Chitoplex (cross-linked N-carboxymethyl chitosan) was used in removing trace metal ions, carrier-free radioisotopes such as cobalt-60 from nuclear effluents, and toxic contaminants such as lead and cadmium from drinking waters [43]. Chitoplex commercial product is a chitin-based polysaccharide product. Results showed that the chelating ability of Chitoplex enhanced by the N-carboxymethyl functional group as well as the cross-linking agent. Furthermore, its performance was best in the temperature interval of 15-60°C, and the gel that was not exposed to drying processes had higher capacity than those dried by thermal or microwave treatment. In addition, results demonstrated that it could eliminate undesirable harmless metals like Fe as well as remove transition metal ions from water. Biodiesel was synthesized using babassu almonds and soybean oils through transesterification reactions using heterogeneous catalysts adsorbed on chitosan biopolymer [44]. Atomic absorption spectroscopy studies was functionalized in the evaluation of the adsorption process of both Cu(II) and Co(II). Results showed that the adsorption process was more efficient for Cu(II) ions. Three hours was enough to attain a maximum adsorption values that were for copper and cobalt cations 1.584 and 1.260 mg.g-1, respectively. The adsorption mechanism proposed that the chelating process may occur through the N and O electron donor centers of the chitosan polymer that was ascertained using infrared spectroscopy. The adsorption abilities of both chitin and chitosan on removing phenol from wastewater of petroleum effluent was investigated [45]. Results showed that the adsorption behavior followed the pseudo-first order kinetics for chitosan biopolymer and pseudo-second order kinetics for chitin. The adsorption processes were optimum at pH range of 2.0-5.0. The resultant adsorption capacities were 1.96 mg/g for chitin and 1.26 mg/g for chitosan. Four adsorption/desorption cycles were performed using ethanol-water (1:1, v/v) as a desorbing medium without a significant decrease in adsorption capacity. A novel flocculants named CATCS of two biopolymers; starch and chitosan is prepared [46]. Their flocculation behavior was investigated. CATCS were evaluated in their capabilities of removing organic contaminants and solid suspending materials. The optimum temperature was obtained at 70oC as well as the optimum ratio was 5: 1 starch: chitosan. CATCS samples possess a positive charge in either acidic or alkaline media. Lowering the temperature of the treated wastewater was confirmed as a favorite condition for the action of CATCS. Nano-hydroxyapatite (n-HAp) as well as chitin modified with nano-hydroxyapatite (n-HAp/chitin) and chitosan modified with nano-hydroxyapatite (n-HAp/chitosan) composites were utilized in the removal of copper ions from aqueous solutions [47]. Many adsorption factors were studied such as contact time, pH as well as selectivity of the metal ion. In addition, thermogravimetric parameters were studied in order to understand the adsorption process. Results showed that the n-HAp/chitosan composite had the highest sorption capacity within 30 min. The sorption capacities during 30min. were in the order of n-HAp/chitosan, n-HAp/chitin composites and n-Hap with values 6.2, 5.4 and 4.7 mg/g, respectively. The sorption process was characterized by being spontaneous and endothermic. Copper removal process seemed to be dependent on adsorption mechanism. The feasibility of using low cost adsorbents in removing organic waste was investigated [48]. Several waste products were used as adsorbents such as chitosan, fruit waste, algae, shell of coconut, rice husk, clays, scrap tires, bark, sawdust, petroleum wastes, fertilizer waste, fly ash, sugar industry wastes blast furnace slag, and seafood processing wastes, seaweed, zeolites, peat moss, red mud, sediment and soil. Adsorption was the main mechanism supposed in removing organic waste. Results proved that the success of the used adsorbents in removing organic waste by about 80-99.9%. Thus, the research had proved the feasibility of converting the waste products to the using of low cost adsorbent materials. Crosslinked microspheres of chitosan natural polymer were utilized as a biosorbent material [49]. The prepared microspheres were used in the removal of perfluorooctane sulfonate (PFOS) pollutants from aqueous solutions. Parameters such as the PFOS concentration, adsorbent and adsorbate sizes as well as the solution pH were investigated. Results demonstrated that the prepared chitosan beads had large adsorption capacities. It reached up to 5.5mmol/g that is larger than those of other sorbents. The removal process was fast at low concentration of PFOS and high pH solutions. The size of the adsorbent microspheres was also effective. The sorption mechanism was reported to depend mainly on the electrostatic and hydrophobic interactions. High PFOS led to the formation of hemi-micelles and/or micelles on the pores of chitosan microspheres. Both fly ash (FA) and zeolite Na-A were modified as adsorbents by chitosan natural polymer [50]. The prepared adsorbents of FA-CS and Na-A-CS were evaluated for the removal of metals ions such as Cu(II), Fe(III), Mn(II) and Zn(II) ions. Factors affecting the removal processes were investigated such as contact time, solution pH, and adsorbent quantity, type of modification by either glutaraldehyde or epichlorohydrin and concentration of metal ions. Results illustrated that the prepared adsorbent samples presented good structural properties. They also provided high adsorption capacities in order of: Cu(II), Fe(III), Zn(II) then Mn(II). The optimum pH was 5.0 and contact time was 120min. Furthermore, increasing the temperature decreased the adsorption capacity. However, chitosan biopolymer needs further modification in order to increase its physical and chemical features.

7. ROLE OF CHITOSAN AND ITS DERIVATIVES

Chitosan in this field could be an effective tool for removal of such pollutants with some handling and/or modifications. Such modification always aims to increase its adsorption capacities and chelation sites. The modification also enhances chitosan solubility in an aqueous environment. Numerous research articles focused on the modification of chitosan using nanoparticles, other polymers, and reactive functional groups. Adsorption ability is tested for chitin as a biosorbent in order to be used rather than chitosan due to its low processing cost [51]. Both chitosan hydrogel/SiO2 and chitin hydrogel/SiO2 hybrid mesoporous materials were synthesized. They obtained by the sol–gel method as a biosorbent against four different dyes; Remazol Black B, Erythrosine B, Neutral Red and Gentian Violet. Results showed that the adsorption processes are pH dependent. The two modified polymer matrices demonstrated better adsorption capacities for dyes than the free polysaccharides. It was found that the chitin containing matrix had similar or higher adsorption capacity than the chitosan one. Results concluded that utilizing chitin modified with silica may be better than chitosan. The sorption capacity of chitosan polymer was improved through modification processes, for removing copper ions [52]. Chemically modified chitosan derivatives like protonated chitosan beads (PCB), carboxylated chitosan beads (CCB) and grafted chitosan beads (GCB) were synthesized. For optimizing the copper removal process, all of contact time, solution pH, and presence of co-anions, various initial copper ions concentrations and temperature factors were studied. They showed good adsorption capacities with values 52, 86 and 126 mg/g for PCB, CCB and GCB, respectively. Therefore, their adsorption behavior is better than that of pure chitosan whose capacity was only 40mg/g. The thermodynamic analysis showed that the sorption processes were spontaneous and endothermic. Silica gel/chitosan composite (SiCS) was prepared via sol–gel method [53]. Copper and lead ions were removed using these composites. Adsorption parameters such as contact time, solution pH, initial ion concentration, presence of co-ions and temperature were investigated. Results ascertained that the adsorption behavior of silica gel/chitosan composite was better than both silica gel and chitosan flakes. The selectivity of the prepared composites for Cu(II) was higher than that for Pb(II) ones. Solutions of pH 5.0 were the optimum ones for removing copper and lead. Being spontaneous and endothermic was also concluded for the process. Adsorption and chelation were the main mechanisms of removal. New hybrid substances of organic-inorganic structures based on chitosan natural polymer and nanosilica particles of (SiO2, TiO2/SiO2 and Al2O3/SiO2 were synthesized [54]. Results demonstrated that the adsorption capacity of both TiO2/SiO2 and Al2O3/SiO2 nanoparticles on chitosan was better than that of SiO2 alone. This seemed to be logic due to presence of more active sites on the surfaces of the mixed oxides compared to that of only SiO2. Samples characterization techniques confirmed that there is a strong interaction between the chitosan and the added oxides which enhance the stability of the prepared samples. Effect of grafted polyethyleneimine (PEI) on the pores of chitosan biopolymers was studied [55]. They were prepared in order to evaluate their abilities on purifying aqueous solutions polluted with the anionic clofibric acid (CA) drug. The impact of the solution pH was evaluated. Results demonstrated that 5% of PEI and six hours were the optimum conditions to produces best adsorbents. SEM images illustrated that PEI molecules were grafted uniformly on the pores of chitosan biopolymer. Images revealed also that they became more mesopores structure. The clofibric acid adsorption process was fast during the first two hours. The PEI-modified chitosan had an adsorption capacity of 349mg/g that was larger than that of individual porous chitosan that was only 213mg/g at pH 5.0. The process was pH-dependent and solutions of pH 4.0 achieved higher adsorption capacities. Analysis studies of surface charge ensured that electrostatic interaction was the main mechanism of CA adsorption. PEI-modified chitosan was proposed to be a potential candidate for the removal of some anionic pharmaceuticals. Modified chitosan with silica was prepared through a sol-gel hybridization reaction [56]. It then functionalized with two functional entities named ethylenediamine tetra acetic acid (EDTA) and diethylenetriamine penta acetic acid (DTPA). They were used for removing Nd (III) rare earth element. Both contact time and solution pH were studied as adsorption factors. Selectivity of the prepared adsorbents was tested by emerging them in a solution containing five rare earth elements; La, Nd, Eu, Dy and Lu. Analysis showed that 30 wt% of the samples was functionalized with organic material and with 70 wt% of silica. pH of 4.0 was the optimum for having the maximum adsorption capacity. The selectivity of DTPA-chitosan-silica was higher than that of EDTA-chitosan-silica against Dy(III) with respect to Nd(III). Chitosan was immobilized on the surface of silica gel in order to remove heavy metals from aqueous solutions [57]. They aimed to find alternatives to the current costly strategies. Glutaraldhyde was used as a crosslinker for chitosan. IR spectroscopy was used to ensure the immobilization of chitosan on silica surface. The formulated adsorbents were functionalized in adsorbing micro quantities of heavy metals such as Zn(II), Cu(II), Cd(II), Pb(II), Fe(III), V(V) and Mo(VI) ions. The prepared composites showed adsorption capacity against the tested heavy metals with maximum values of 0.46 mmol/g for zinc, 0.31mmol/g for vanadium and 0.02mmol/g for molybdenum. Few minutes were enough to obtain a maximum adsorption capacity for all the studied ions. A hybrid nanocomposite material was synthesized from the interaction between chitosan biopolymer and tetraethoxysilane (TEOS) using the sol-gel method [58]. Furthermore, microspheres of chitosan using glutaraldhyde as a crosslinker were made. A comparison between the prepared samples regarding their ability of adsorbing micro quantities of V(V), Mo(VI), and Cr(VI) oxoanions was held. The comparison showed that the synthesized chitosan-silica composite had better adsorption capacity than the initial chitosan with respect to the studied oxoanions. Chitosan composites were prepared using silica (SiO2) and alumina (Al2O3) [59]. The physiochemical properties of chitosan composites were investigated such as Carbon yield (%), moisture content, pH, acidity and basicity, zero point charge, Boehm's titration and Iodine number. They found that the iodine number of chitosan modified silica was 2743.6mg/g and higher than that of chitosan modified alumina which equaled 2121.5mg/g. Similarly, the carbon yield of the former was 91.6% and greater than the later that was 85.2%. Results showed that the higher the iodine number is, the greater the yield will be. Furthermore, results ensured that the preparation procedure had a significant impact on the morphology of the formulated beads where higher basicity solutions yielded spheres of more irregular spherical shape. Therefore, the resultant data supported the use of the prepared composites in wastewater treatment processes. Chitosan was utilized with alginate natural polymers in the modification of metal-organic frameworks (MOFs) named MIL-101 Cr [60]. The prepared adsorbents were used in purifying aqueous solutions contaminated with pharmaceutical pollutants named ibuprofen (IBP), benzoic acid (BA) and ketoprofen (KET). Effects of solution pH, ionic strength and isotherm data were recorded. Results reported that the composite beads of MIL-101(Cr)/chitosan had the highest adsorption capacities with respect to others. They removed the selected PPCPs in the order of KET, IBP and then BA. X-ray photoelectron spectroscopy technique (XPS) ensured that electrostatic interaction took place between the protonated amine groups as well as the Cr center of the sorbent samples with deprotonated carboxyl one of the pollutants. It was one of the main proposed interaction mechanism. In addition, π-π interaction had a significant influence on the adsorption of the three contaminants according to adsorption analysis as well as π energy.

8. ROLE OF MOLECULAR MODELING

Molecular modeling, besides other experimental techniques, was utilized to study biopolymers. Computational physics and molecular modeling can describe the various chemical interactions qualitatively and also quantitatively. They are usually conducted to understand the interaction mechanisms. However, a limited number of research articles focused on studying the theoretical behavior of chitosan with various structures. Few numbers of papers have focused on optimizing structures of chitosan and other polymers and studying their physical, electronic and thermodynamical properties. The interaction between chitosan and hydroxyapatite was investigated using molecular modeling [61]. Electronic properties of their interaction were calculated using semiempirical quantum mechanical calculation at PM5 method. Moreover, another model was constructed using DFT at B3LYP with 3-21G** basis set. Results showed that chitosan interacts with hydroxyapatite physically through hydrogen bonding with Ca^{2+}, PO_4^{3-} and OH^- of hydroxyapatite. Interacting chitosan with hydroxyapatite reduced their HOMO/LUMO binding gap energy. The calculated thermodynamic parameters suggested the formation of stable blends. The obtained results of the total dipole moment and band gap energies also suggested the suitability of these blends for biomedical applications. Semiempirical quantum mechanical calculations were utilized at PM3 method to study cellulose and chitosan up to 8 units as individuals and as chitosan/cellulose blends with different ratios [62]. Total dipole moment and HOMO/LUMO energy were calculated. The change in the calculated total dipole moment and HOMO/LUMO energy suggested that cellulose/chitosan blend is more reactive than individuals. Furthermore, their reactivity increased as a result of introducing titanium dioxide (TiO_2) and zinc oxide (ZnO). The addition of TiO_2 and ZnO to the blend increase the total dipole moment and lower the HOMO/LUMO energy that made them more stable and more reactive with the surroundings. They recommended their proposed blends for biological as well as environmental applications through the cross-linking (OH and NH_2) as well as having high surface area provided the introduced metal oxide is in nano size. A model is constructed in order to simulate the adsorption of diclofenac on chitosan hydrogel [63]. The built model was optimized using the semiempirical quantum mechanical calculation at PM3 model. Some thermodynamical parameters such as Gibbs free energy as well as some QSAR properties such as partition coefficient, surface area, volume, mass and molecular vibrations before and after adsorption were calculated. Results demonstrated that adsorbing diclofenac in chitosan hydrogel was confirmed by the value of the partition coefficient which illustrated an affinity to the water molecules involved in the hydrogel. In addition, the optimization geometry proposed the formation of hydrogen bonds between chitosan and diclofenac and it had a significant role in its adsorption. Interaction probabilities between chitosan monomer and ibuprofen molecule were studied [64]. Five possibilities were proposed in either presence or absence of water; one chemical probability and four physical ones. The calculations were carried out using PM6 semiempirical method. Some physical, electronic, thermodynamical and QSAR properties were calculated. Results indicated there are variations in the partial charge is followed with increase in total dipole moment. The resultant structures seemed to be more reactive than individual ones. The interaction is most probable to occur through OH…HO physical bond that is ensured by both total dipole moment and HOMO/LUMO band gap energies. In addition to the proposed articles that were interested in only either the experimental part or the theoretical one, there are some papers studied the interaction of chitosan with several structures from the two points of views; theoretical as well as experimental ones. Their strategy depends on constructing a molecular model describing their own interaction due to the mechanism point, then carrying out an experiment to evaluate the resultant theoretical model. Casting method was utilized in order to prepare chitosan/starch and chitosan/gelatin films of different ratios [65]. Results of FTIR proved that the polymers interacted together through hydrogen bonding between the amine (NH_2) and carboxyl (COOH) groups at their terminals. Moreover, a molecular model was constructed at PM3 semiempirical quantum mechanical calculation. The vibrational IR frequencies as well as total dipole moment and the HOMO/LUMO band gap energy were calculated. Results of the constructed model were in agreement with spectroscopic data. They also indicated that blending chitosan with starch and gelatin slightly decreased the HOMO/LUMO band gap energy and increased the total dipole moment reflecting increased reactivity. UV-vis spectroscopy studies showed the availability of using chitosan/starch blend as a glycine sensor. Finally, the sensing properties of chitosan/starch blend were improved by introducing 5 nm size TiO_2 into the blend. The solvent effect was studied for many solvents on the [phthalic anhydride-chitosan] monomer [66]. The studied solvents are named dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF), tetrahydrofuran (THF), 1,2-ethylene diamine (EDA), ethylene-carbonic acid (ECA) and propylene-carbonic acid (PCA). Some physical parameters including dipole moment, HOMO, LUMO, hardness (η), electronic chemical potential (μ) and global electrophilicity index (ω) were calculated by semiempirical quantum mechanical calculation using PM3 method and Ab intio level using HF/3-21G and DFT/B3LYP/3-21G methods. The resultant calculated parameters using different theoretical methods were compared together and also with experimental ones. All calculated results demonstrated good agreement with experimental ones. Less polar solvents like DMSO, EDA and DMF could solubilize the polymer. Experimentally, the N-phthaloyl chitosan polymer dissolved in the mentioned solvents. Finally, the performed calculations were useful for selecting the best solvent to solubilize the polymer of [phthali canhydride-chitosan] monomer. Polymer blends of alginate and chitosan biopolymers were prepared and characterized in order to act as a drug delivery carrier for one of the antidepressant drugs named Venlafaxine XR [67]. The research aimed to overcome the side effects of having free drugs. QSAR studies of chitosan and alginate structures were carried out. FTIR results revealed good entrapment of the drug into the formulated polymeric matrix. Results of QSAR referred to the presence of a strong electrostatic interaction in the nanoparticles. Encapsulation of the drugs into a nanoscale enhances their dispersal and absorption rate. Molecular modeling was utilized in studying the possible applications of chitosan blended with dried water hyacinth plant sample to form microsphere to remove pollutants [68]. A model was built up to simulate the modified plant as 3 cellulose units, one lignin and some metal oxides named CaO; FeO and $Al(OH)_3$ are attached through O-Linkage. Furthermore, microspheres of dried water hyacinth and chitosan were synthesized in the laboratory following self-assembly method relying on the constructed model. Formation of a composited was verified through both FTIR spectra and SEM micrographs analysis. The resulted FTIR spectrum of microspheres exhibited only the characteristic bands for the individual water hyacinth and chitosan and no new ones as well as the SEM micrographs of microspheres showed that the fibers of water hyacinth are imbedded in the crosslinked chitosan matrix which gives strong evidence that the formed material is a composite. Results obtained from the model indicated the ability of the blend to remove inorganic pollutants from wastewater due to the unique hydrogen bonding and high total dipole moment. Experimental data confirmed the theoretical assumptions where the adsorption process was very fast and attained equilibrium after only 30 minutes.

9. RECENT DEVELOPMENTS

Again starting in medical filed one can find many recent developments in the biomaterial research especially those depending on chitosan. Tissue engineering with biomaterials is not really new route but the most recent trend is the utilization of conductive biomaterials, especially those have biocompatibility which is now widely used to fabricate in vitro platforms for differentiation of progenitor cell population as well as implantable tissue engineering scaffolds [69]. Using biomaterials in cardiac heart treatment is very important especially for making new tissue for muscle treatment. Cardiac cell therapy is very important for improving heart function and especially of the permanent failure of muscle functions. Embedding cells into 3D biodegradable scaffolds may better preserve cell survival and enhance cell engraftment after transplantation, consequently improving cardiac cell therapy compared with direct intramyocardial injection of isolated cells [70]. Nowadays it is well known that the disease which is affecting the cornea of the human eye is the main reason for blindness all over the world [71]. Up to date, the amniotic membrane from pregnant woman after birth that is termed AM is considered the main source used clinically in different hospital for corneal regeneration. Donor-dependent differences in the AM could result in variable clinical outcomes. This problem could be overcome, and then the proposed biomaterials are currently under investigation for corneal regeneration in vitro and in vivo. Chitosan as well as other biopolymers may enhanced by the introduction of small amount of nanoscale materials in the form of nano metal oxide. Furthermore, chitosan has been reported to disperse and stabilize several nanoparticles to produce more potent antimicrobial nanocomposites [72-73]. Chitosan-based nanocomposites show potential applications in the field of wastewater treatment based upon its potential antimicrobial benefits [74]. But how to avoid environmental hazardous if it exists for chitosan nanocomposites according to nanomaterial toxicity in-vitro and in-vivo. It is important to evaluate the biological effects of nanoparticles [75-76]. The aquatic environmental risk assessment for chitosan/silver, copper and carbon nanotube were studies [77]. It is indicated that, loading of the chitosan matrix with small concentrations of nanoparticles with different dimensional forms improves the potency of their antimicrobial properties. However, aqueous exposure to these preparations still has toxicological effects on fish. Several parameters, including oxidative stress, DNA fragmentation, pro-inflammatory cytokines and pathological alterations, exhibited acute toxicity in exposed fish. Accordingly, chitosan-based nanocomposites, fabricated and applied in non-leaching forms to avoid the release of nanoparticles to the surrounding environment, is recommended to decrease the environmental risk of these nanocomposites while maximizing the utilization of their antimicrobial effects.

Multi-wall carbon nanotubes (MWCNT-COOH) with chitosan (Chi) has been investigated for the removal of picric acid from aqueous solutions. Different factors affecting the sorption process were studied [78]. Results indicated that picric acid can be desorbed up to 90% at pH = 9, the chitosan nanocomposite could be reutilized up to 5th cycle of regeneration.

Chitosan-TiO_2 nanocomposite (CTNC) was prepared for the selective and quantitative removal of Rose Bengal dye from industrial wastewater [79]. The prepared composite indicated high performance according to its high surface area (95.38m2/g) with relatively uniform mesoporous channels that allowed an exceptional uptake of the dye (qm = 79.365 mg/g) and reflected the high selectivity of the composite as compared with pure chitosan. The dye uptake was investigated using Freundlich, Langmuir, Dubinin Radushkevich and Temkin models. The kinetics of removal was explored by pseudo-first, pseudo second order, Elovich and Weber-Morris models. The Experimental data fitted well into pseudo-second order model, and much well with the Langmuir isotherm confirming the formation of a monolayer of dye molecules.

Dye removal and/or degradation become one of the major challenges to minimize environmental damages made by the drastic development of industries that disposes dye effluent into the water bodies without adequate treatment. In this sense, chitosan derivatives and composites are among so called green materials that offer a sustainable environment, so that it received a lot of attention because they are environmentally friendly and biodegradable. Removal and/or degradation of organic dyes from wastewater by chitosan nanocomposite as well as other biopolymer nano based materials is still a hot topic of research work could be reported in may recent research work [79-86]. According to low cost and eco-friendly these class of biopolymers, composites are of concern in other contaminants.

Nowadays hospitals, industries, and domestic activities leading to a new class of pollutants called emerging pollutants. Miscellaneous drugs and pharmaceuticals residues Proteins; antibiotics Proteins residues. Are considered among the emerging pollutants. For remediation of such pollutants, a new generation of adsorbates are reviewed [87].

Pesticides are which are widely used in agricultural fields to protect the crops from various diseases and pest damages are considered among the most harmful residues in the environment. Nanomaterials show potential to remediate pesticides from the environment. Biopolymers such as chitosan are also stabilizing the use of nanomaterials and facilitate its applications in the removal of the complex structure from the environment such as pesticides [88].

Water pollution is a major environmental problem according to rapid industrialization and indiscriminate disposal of toxic metal ions. The existence of toxic metal ions in water has many harmful impacts as they are accumulated in living organisms. Removal of metal ions from the aquatic environment is a kind of scientific challenge [89-92]. ZnO-Chitosan core shell nanocomposite shows potential applications in the removal of toxic metal ions such as Pb(II), Cd (II) and Cu(II) from wastewater [93].Chitosan/graphene oxide nanocomposites are modified to remove Cu from aqueous solution [94].

Nano 5%Bt/CS were prepared from the raw materials and used as a biosorbents for the removal of chromium ions from both aqueous solution and a real rejection of tannery industry [95]. The adsorption kinetics of Cr(VI) ions onto the adsorbents were described by the pseudo second order model, and the experimental isotherms data were described by the Langmuir and the Redlich-Peterson models. The adsorption capacities of Cr(VI) ions at pH = 5 and at T = 298 K were found equals to 304mgg−1 and 223mgg−1 for CS and nano 5%Bt/CS, respectively [96].

The work is further modified to study the performances of local chitosan and its nanocomposite 5%Bentonite/Chitosan in the removal of chromium ions (Cr(VI)) from wastewater [97]. Both spectroscopic and molecular modeling analyses dedicate chitosan as a membrane working as oil carrier [98]. Another application for chitosan as to be enhanced and act as radiation protection agent [99]. Also it could be interface to modify the surface of silicon to act as functionalized silicon substrate for DNA [100]. Chitosan among some biopolymer blends could be applied as bio-sensor [101]. The interaction of F - ions with pristine and protonated chitosan using both experimental and molecular modeling at DFT level is tried. The overall aim is to understand the structure, reaction mechanism, and stability of the complex formed and the efficiency of adsorption [102-104]. Chitosan could be also applied to modify the surface of poly (lactide-co-glycolide) nanoparticles to act as on-demand drug delivery system [105]. Chitosan/gelatin is prepared as nanofibrous scaffolds for application in tissue engineered field [106]. Further modification could be achieved for carboxymethyl chitosan/forsterite to be applied as bone tissue engineering scaffolds [107].

10. CONCLUSION

Biomaterials continue to attract researchers in many areas of research. Chitosan one of this class of materials. These materials are easy to handle and could be modified to overcome their drawbacks. One of these modifications is to inset nanomaterials forming so called biomaterials nanocomposites.

It could be concluded that polymeric nanocomposites have been widely applied to many areas not limited to biological applications, engineering, homogeneous and heterogeneous catalysis, sensors, filter applications, and optoelectronics. These materials are of extra features as compared with conventional materials, such as it could be processed with low energy consumption, and the most important aspects are their biodegradation which facilitates the process of its recycling. These polymeric nanocomposites show potential to be used in environmental applications, not only because they offer large adsorption capacity, but also due to their simple operation, high stability, and selective sorption toward a wide range of pollutants in wastewater. Polymeric nanocomposites pave the way toward the existence of eco-friendly, high performance materials also described as cost effective materials. The importance of these materials is increasing abundantly to replace conventional materials which are considered as nonrenewable and highly cost.

11. REFERENCES

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