ПЛАЗМЕННО-РАСТВОРНАЯ ОБРАБОТКА ПРИРОДНЫХ ПОЛИМЕРНЫХ МАТЕРИАЛОВ

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Неравновесная низкотемпературная плазма атмосферного давления является высоко реакционноспособной средой, которая позволяет модифицировать природные материалы экологическим способом. В данной работе рассматривается область плазменно-растворной модификации материалов на основе полимеров, полученных из природных источников. Рассмотрены типы плазменно-растворных систем с точки зрения эффективности генерации активных частиц, их транспорта и взаимодействия с макромолекулами. Регулируемая модификация растений (береза, ива, побеги бамбука и винограда; ячмень, рис и солома рапса, многолетние травы), водорослей, побочных продуктов растительного происхождения и отходов (опилки, лубяные волокна, ореховые скорлупы, семена, кожура, жмых и выжимки), полимеров растительного происхождения (целлюлоза, гемицеллюлоза, лигнин, крахмал, альгинат натрия) и материалов на основе полимеров животного происхождения (хитозан, коллаген, желатин) путем плазменной обработки в растворе сравнивается с традиционными химическими методами. Также рассматривается синтез нанобиокомпозитов с расширенными функциональными возможностями.

Ключевые слова: растения, водоросли, лубяные волокна, природный полимер, плазменная обработка в растворе, плазма в жидкости, высоковольтный электрический разряд

SOLUTION PLASMA PROCESSING OF NATURAL POLYMER-BASED MATERIALS

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Non-equilibrium low-temperature atmospheric pressure plasma is a highly reactive medium that allows for the ecofriendly modification of nature-derived materials. This work reviews the field of liquid phase plasma modification of polymer-based materials derived from natural sources. Types of solution plasma systems are considered with respect to the efficiency of the generation of active species, their transport to and interaction with macromolecules. Tunable modification of plants (birch, willow, bamboo and vine shoots; barley, rice and rapeseed straw; perennial grasses), algae, plant-derived by-products and wastes (sawdust, bast fibers, nutshells, seeds, peels, press-cake and pomace), plant-derived polymers (cellulose, hemicellulose, lignin, starch, sodium

alginate) and animal-derived polymer-based materials (chitosan, collagen, gelatin) by solution plasma treatment is compared to conventional wet chemistry methods. Synthesis of nano-biocomposites with advanced functionalities is also considered.

INTRODUCTION

Plant- and animal-derived commodities have been known to humankind for ages: flax textiles were manufactured in the territory of modern Georgia 30 000 years ago [1], the cultivation of hemp in Southeast Asia, the manufacturing of papyrus from sedge fibers in Egypt and the production of silk in China date as far back as the 4th millennium BCE [2-4]. Throughout history, humans have also rationalized technologies for the production of goods from natural sources which included the fabrication of finished products based on plant- or animal derived polymeric materials (natural polymers). The oldest wool garments date back to at least the 1st millennium BCE [5]. Starch was known in Europe about 30 000 years ago [6]. The invention of paper in China in the 2nd century BCE is another hallmark of the production of natural polymer-based goods [7].

Nowadays, production of natural materials is supported by the necessity to solve the issues of renewability and sustainability. Taking this into account, the United Nations General Assembly declared the year of 2009 as the International Year of Natural Fibres [8]. The worldwide production of natural fibers reached 30 million tons in 2016 and about 60 million households were involved in this production as reported by Discover Natural Fibres Initiative [9]. It is generally recognized that such mass market production should be accompanied by the development of innovative processing methods that will allow for clean, eco-friendly solutions. Non-equilibrium low-temperature plasma may prove to be a medium of choice for this purpose.

Non-equilibrium low-temperature plasma processes find numerous applications including synthesis of materials with unique properties: effective catalysts, organic semiconductors, diamond-like coatings, biologically active materials, etc. An intensive research was performed also on the modification of polymeric materials, including natural polymer-based materials, using non-equilibrium plasma in the gas phase under reduced pressure. The high capital cost of vacuum equipment and the complexity of combining vacuum operations with traditional wet chemical processes hindered the use of low-pressure plasmas for the high throughput modification of natural materials.

Atmospheric-pressure discharges offered the advantage of the treatment under ambient conditions and significant efforts were invested into this field. Having started from the control over the wettability, atmospheric pressure plasma treatment now aims at more challenging tasks that include, but are not limited to, the production of shrink-resistant and anti-felting wool [10], itch-free wool for comfortable contact with the skin [11], shedding-free angora apparels [12], biodegradable apparel from banana fibers with improved spinnability [13], sisal fiber reinforcing elements [14], decorative fading of cotton denim [15], antibacterial cellulose [16], etc.

High chemical activity of gas phase plasmas is typically opposed by a relatively low efficiency and selectivity of the targeted action on the micro- and nanoporous natural polymer-based material being processed [17]. The limited efficiency is associated with a short lifetime of plasma-generated active species that become lost/quenched before they may reach the inner surface of tiny capillaries. Thus, the inner cavities of different size-scales are not treated uniformly. The limited selectivity is an unwanted consequence of high chemical activity of plasma: the rates of the generation of active species are very high in the gas phase. Their chemical reactions with macromolecular compounds are also fast and their rates are not very different for different species. Thus, different components of natural polymer-based materials are treated with comparable rates, limiting the selectivity of the action.

Atmospheric-pressure plasma was also adapted to the treatment of liquids. One of the first reports can be found in a letter of an American naturalist Timothy Lane addressed to Benjamin Franklin in 1767, in which

he described the experiments with the spark discharge not only in the air, but also in water and other liquids [18]. In 1815, Singer and Crosse reported on explosions occurring between wires positioned co-axially in a water-filled metal tube and powered from a battery of Leiden jars [19]. The following centuries witnessed further research on transformation of electrical energy into mechanical (electrohydraulics) in electrical discharges in liquids [20, 21] or on electrochemistry [22, 23]. However, it would not be a great exaggeration to say that it was only at the beginning of the 21st century that plasma in liquid has emerged into a separate field of scientific investigation. Strong interest in this topic is evidenced by an increasing number of international scientific meetings held in the late years (for example, the workshop Gas/Plasma–Liquid Interface: Transport, Chemistry and Fundamental Data in 2014, and International Conference on Plasmas with Liquids in 2017). In 2013, a dedicated European Cooperation in Science and Technology (COST) action named Electrical Discharges with Liquids for Future Application was organized that involved 27 participating countries [24].

It has to be noted that conventional terminology has not so far been established, evidently because of the relative novelty of the field. Different names have been suggested that include plasmas in/with liquids, glow discharge electrolysis plasma (GDEP), high voltage electrical discharge (HVED) and some others. Herein, we opt for the term Solution Plasma Processing (SPP) introduced by a group from Nagoya University [25], which seems to be the most universal for the description of various types of electric discharges in liquids.

SYSTEMS FOR SOLUTION PLASMA PROCESSING

The interaction of the plasma with the liquid phase can be organized in a number of ways. The electric discharge can be ignited in the gas phase above the liquid surface or it can be ignited directly in the liquid phase. For the gas-phase plasma, the liquid is treated by the discharge, which can be maintained between the electrodes located in the gas phase. However, another arrangement is used more frequently, in which the treated solution itself serves as one of the electrodes (Fig. 1a). In this case, the current passes through the electrolyte solution, which significantly changes the properties of the plasma-liquid interface [17, 26, 27]. Plasma can be created both in vapors above the surface of the liquid and in the vapor bubble that occurs inside the liquid phase as a result of overheating instabilities or due to gas release as a result of electrochemical processes at the electrodes. The applied voltage can be constant (several kV) or pulsed, typical values of the discharge current range from units to hundreds of mA. Air or other gases (Ar, N$_2$, He, N$_2$O, CO$_2$) can be used as plasma-forming media.
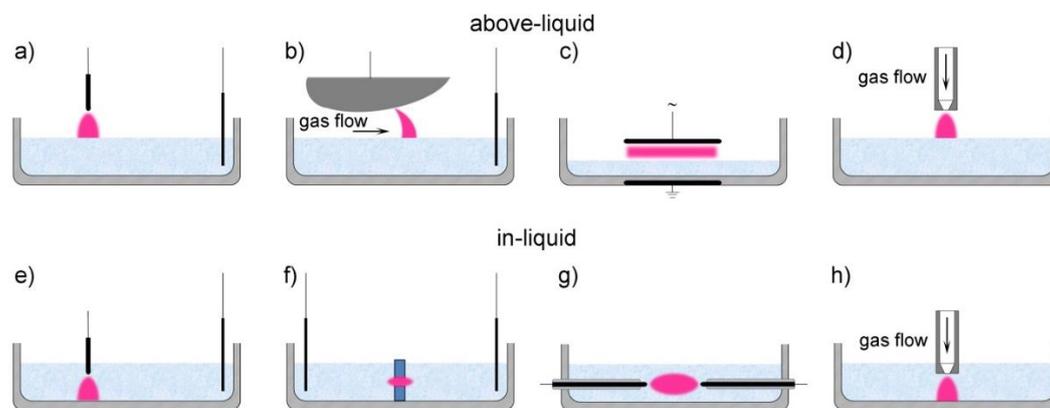

Fig. 1. Schematics of typical experimental arrangement used for solution plasma processing of natural polymer-based materials. The gas-phase plasma contacts the surface of the liquid: a) discharge with liquid electrode; b) gliding arc; c) DBD; d) above-liquid plasma jet; or the discharge is ignited directly in the liquid phase: e) point-to-plate electrode discharge; f) diaphragm (capillary) discharge; g) point-to-point electrode discharge; h) in-liquid plasma jet

Рис. 1. Схема типичных экспериментальных установок, используемых для плазменной обработки растворов материалов на основе природных полимеров. Газофазная плазма контактирует с поверхностью жидкости: a) разряд с жидким электродом; b) скользящая дуга; c) диэлектричесий барьерный разряд; d) надводная плазменная струя; или разряд зажигается непосредственно в жидкой фазе: e) разряд электрода от точечного электрода к пластине; e) диафрагменный (капиллярный) разряд; f) разряд между точечными электродами; g) плазменная струя в жидкости

Gliding arc is another type of the non-stationary discharge, which is excited in a gas stream directed parallel to the surface of the solution (Fig. 1b). Typically, the surface of the liquid serves as a cathode and the metal anode has a shape that provides a gradual change in the inter-electrode distance along the gas stream [17, 28, 29]. When a constant voltage of up to 10 kV is applied, the discharge is ignited in the region

of the minimum distance between the electrodes. The discharge begins to move under the action of the gas flow (gliding) until it extinguishes due to an increase in the inter-electrode gap. The phenomenon is repeated with a frequency that depends on the gas flow rate. Typical discharge current values reach 100 mA.

Dielectric Barrier Discharge (DBD) can be also adapted for solution plasma processing (Fig. 1c). In this case, the solution is poured onto an electrode protected by a dielectric barrier (quartz, alumina). A counter-electrode is placed at a certain distance from the liquid surface so that a several mm gap is present in between. The DBD is excited in this gap by applying kV voltages of audio frequency in He (homogeneous discharge, yet expensive) or in air (filamentary discharge, low-cost) and other gases [30, 31].

Atmospheric pressure plasma jet is another option that allows for the plasma treatment of the liquid surface (Fig. 1d). The discharge is ignited typically in a hollow tube with specifically configured electrodes installed inside or wound around. Several kV audio frequency voltage is supplied between the electrodes and the plasma is maintained in the gas flow [32, 33]. The effluent gases can be directed onto the liquid surface either as plasma or as its afterglow, depending on the distance between the jet nozzle and the treated surface. It is worth noting that the electric current does not flow through the solution in this case and the transfer of active species from the plasma to the liquid is given by the convection/diffusion mechanisms.

The second group of the electric discharges for solution plasma processing involves systems in which plasma is formed inside the liquid. This configuration allows materials to be processed by combining the physical effects produced by plasma itself and chemical effects induced in plasma-activated solution which can be advantageous from the point of view of chemical applications. In-liquid discharges are realized by placing the electrodes directly into the liquid phase. The plasma can be excited in the vicinity of one electrode if the area of the counter-electrode is larger (point-to-plate configuration) and relatively low voltages (less than 1 kV) and currents (10 mA to 2 A) are applied (Fig. 1e). Both DC and AC sources (for example, with a frequency of 50 Hz) can be used to excite such a discharge [34]. Higher energy can be also supplied to the plasma by creating a more intensive electric field (up to 40 kV voltage and 10 kA current) between the point and the plate electrodes (underwater arc discharge, also known as HVED). In this case, sparks propagate and occupy the entire liquid volume between the electrodes. The discharge is also accompanied by the formation of gaseous cavities, the development of strong turbulence and the propagation of intensive shock waves [35]. It should be mentioned also

that this type of the discharge is thermal, that is the conditions of non-equilibrium plasma are not fulfilled in this case.

Intensive electric field can be created under less energetic conditions by introducing a diaphragm between the electrodes or simply if the electrodes are placed at a closer distance from each other. In the former case, the electrolyte solution is divided into two parts by a dielectric membrane with a small aperture (Fig. 1f). The application of voltage between the electrodes located on both sides of the membrane causes the passage of electrolysis current, the density of which is maximal within the diaphragm. When a certain critical current density is reached, overheating instabilities develop within the diaphragm and a vapor bubble forms, which breaks the electrical circuit. If the total potential difference at the boundaries of the bubble is insufficient for electrical breakdown, the bubble collapses and the process is repeated. However, at a sufficiently large potential difference, electrical breakdown occurs. The pressure in the diaphragm area rises sharply and a shock wave arises, propagating in both directions from the diaphragm. As a result, a quasi-periodic diaphragm discharge appears in the solution. The voltage of up to 5 kV and the current of up to 50 mA are typical conditions reached in the diaphragm discharge [17, 34, 36].

If two electrodes are brought closer to each other, the presence of the diaphragm for the field enhancement is not required anymore and the discharge can be operated at about 1 kV voltage and 10 A current (Fig. 1g). Bi-polar pulsed excitation is reportedly advantageous for the generation of stable plasma [25]. At an inter-electrode distance of several mm, two plasma zones are formed in the vicinity of each electrode whereas a single plasma region is created at the distance < 1 mm [37]. An important factor here (and for the diaphragm discharge as well) is that the plasma has a smaller volume limited by the geometry restrictions.

GENERATION OF REACTIVE SPECIES IN SOLUTION PLASMA SYSTEMS

The detailed description of the physical and chemical processes occurring upon interaction of plasmas with liquids falls far beyond the scope of this manuscript. The reader is referred to several reviews that appeared in the last years [38, 39]. Nevertheless, it is worth mentioning that collisions of energetic electrons with molecules play a crucial role in the formation of active species in the solution plasma processing. The set of most important species formed during this treatment is close to that observed under glow discharge conditions in humid air or in water vapor: (V)UV photons, ions, reactive oxygen and nitrogen species (ROS, RNS) and H atoms. Of all the ROS, OH radicals and

H_2O_2 are presumably the most frequently studied species in terms of the chemical interactions with natural polymer-based materials. The OH radicals are created from dissociation of water molecules either by direct electron collisions or via secondary reactions. They have extremely strong oxidizing potential and are often considered as the major species that induce chemical transformations in solution plasma-treated organic compounds. However, the lifetime of the OH radicals in the liquid phase is very short, being in the range of 10^{-6} s and less, which means that they must be generated in close proximity (better *in situ*) with the material to be treated. One of the well-known channels of the OH radical quenching is the recombination of two OH radicals with the formation of H_2O_2, which is characterized by substantially longer lifetimes. H_2O_2 may decompose by a variety of pathways; in particular, the generation of molecular oxygen or OH radicals is often reported. Thus, H_2O_2 can serve as a long-term stock of ROS for the treatment of organic matter, including natural polymer-based materials.

Plasma chemistry is also combined with a plethora of physical phenomena including transport of species, development of shock waves, heating, etc. Altogether, high activity of plasmas mediated by physical and chemical phenomena occurring in liquid may provide synergistic effects for controllable modification of the structure and chemical composition of various materials.

The idea seems to be relevant for commonly hard-to-modify natural commodities, especially taking into account that a great number of today's technologies utilize liquid phase for their processing. A rapidly increasing interest in solution plasma processing of nature-derived polymer-based materials can be illustrated by Fig. 2 where the number of the scientific papers published on this topic and cited in this review is presented. Evidently, the outburst of the publication activities occurred around 2012 and since then the number of papers has been increasing rapidly.

SOLUTION PLASMA PROCESSING OF PLANT-DERIVED POLYMER-BASED MATERIALS

Markedly, the already mentioned Lane-to-Franklin letter might be the first report ever on the solution plasma processing of plant-derived matter. Mr. Lane was fascinated by explosions produced by spark discharges and experimented with different media filling the inter-electrode gap. For the experiment with water-filled phials, he wrote: "When the phial is not broken by the electric stroke, the agitation of the water may be sensibly observed at the instant of the explosion, and the electric spark evidently seen to pass through the water, from the point of one wire to the other", and also: "If a mucilaginous vegetable paste is used, as wheat-flour and water, etc. the experiment will appear the same" [18]. Paying tribute to these great pioneering studies, it must be admitted that the importance of the Lane's experiments for the modification of nature-derived materials remained unnoticed either by Lane himself or by Franklin, or by their followers until the mid-20th century when it was realized that electro-hydraulic phenomena can be used for crushing of organic materials, for complex processing of agricultural products as well as for the preparation of feed for livestock.
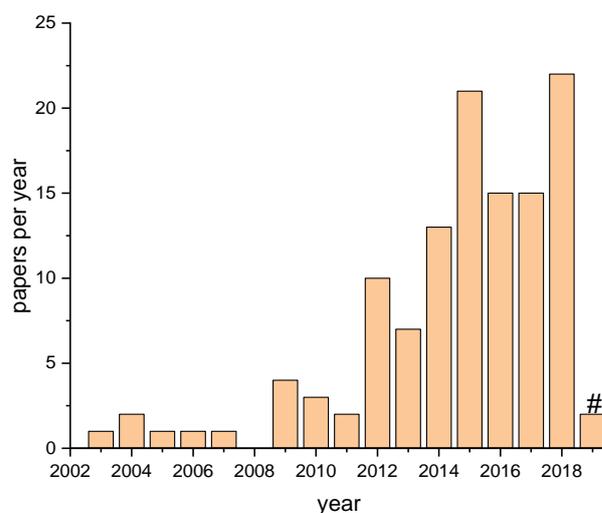

Fig. 2. The number of the papers on solution plasma processing of nature-derived polymer-based materials cited in this review in dependence on the publication year. # January, 2019

Рис. 2. Количество работ по плазменно-растворной обработке материалов на основе полимеров природного происхождения, цитируемых в этом обзоре в зависимости от года публикации. # Январь 2019 г.

Cells of many plants and algae contain biologically active substances (vitamins, phytoncides, microelements, etc.) that regulate vital processes of the body. They also contain other useful nutrients such as proteins, fats and carbohydrates. Furthermore, plant and algae feedstocks may serve as important resources for the production of bio-ethanol and other chemicals with the purpose of limiting the consumption of fossil fuels. However, the useful plant components are often enclosed in a solid lignocellulose casing, which makes them hardly accessible (Fig. 3). Lignocellulose is a composite biomass consisting mainly of cellulose, hemicellulose and lignin, with other components present in minority. It is the high content of lignin and cellulose that explains the mechanical rigidity of plants and provides protection to their useful compounds.

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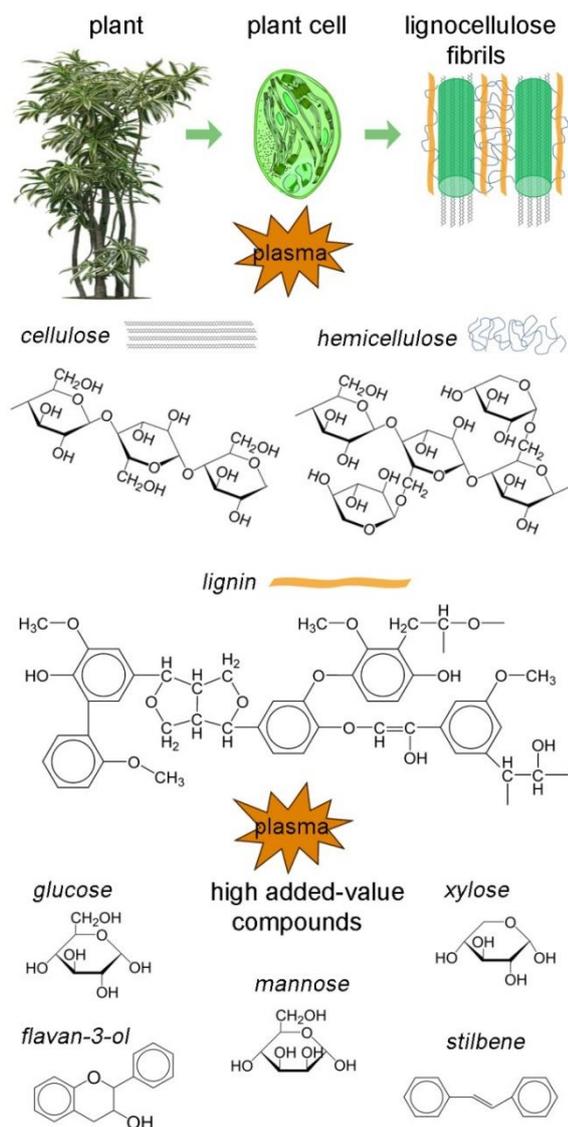Изв. вузов. Химия и хим. технология. 2019. Т. 62. Вып. 7

Fig. 3. Scheme of solution plasma processing of plants. Cell walls of plants contain lignocellulose – an inter-connected composite biomass consisting of cellulose, hemicellulose and lignin. Solution plasma processing facilitates the separation of these components and may further convert them into high added value compounds

Рис. 3. Схема плазменно-растворной обработки растений. Клеточные стенки растений содержат лигноцеллюлозу - взаимосвязанную композитную биомассу, состоящую из целлюлозы, гемицеллюлозы и лигнина. Плазменная обработка в растворе облегчает разделение этих компонентов и может дополнительно превращать их в соединения с высокой добавленной стоимостью

Thus, the main aim of the treatment of plant-derived materials is to separate lignin and cellulose from other components so that they are available for further processing. The constantly growing requirements for the environmental safety of technological processes, and the need to obtain a more complete separation of the plant components, not provided by tradi-tional chemical methods, stimulate the search for fundamentally new solutions to the problem. From this point of view, solution plasma processing seems very promising for the modification of plant-derived materials.

Plants

The first research on deliberate in-liquid plasma delignification of livestock fodder and destruction of cells in other plant- and animal-derived tissues were carried out in the second half of the 20th century [40, 41] (Table 1). Solution plasma processing of birch and willow shoots and of barley straw was suggested with a purpose of taking advantage of an electrohydraulic effect occurring when pulsed arc discharge is generated in liquid (up to 50 kV voltage). The formation of shock waves resulted in an increase of the mass content of soluble and reducing sugars in the samples by 23, 30 and 73%, respectively. The increase of easily digestible nutrients was reported to enhance the nutritional value of the fodder, and also allowed for its further use as a substrate for growing yeast and non-pathogenic mushrooms in the microbiological industry [21, 42]. The experiments were performed with long-term feeding of dairy cattle by the paste made of solution plasma-treated birch and willow shoots. The milk productivity of animals was 11-12% higher than that of the control group whereas their general physiological state remained at the control level.

Recently, more sophisticated studies were performed that utilized in-liquid pulsed arc discharge (HVED, up to 40 kV and 10 kA) for the solution plasma processing of vine shoots and rapeseed straw, agricultural by-products typically used as a source of heat from combustion or for animal feeding. However, they can be also considered as the feedstock for high added-value compounds such as polyphenols, proteins and lignin. Solution plasma processing was shown to be effective in terms of increasing of the polyphenol and protein extraction yield, especially if compared to other methods of ultrasonic and pulsed electric field treatment [43]. The generation of H_2O_2 was detected, the concentration of which increased with the energy input, yet without any polyphenol degradation [44]. It was also found that preliminary grinding of the vine shoots promoted the cellular damage, however only to a certain level [45]. Finally, it was suggested that a sequential treatment by the solution plasma processing followed by enzymatic hydrolysis and alkaline delignification was the most efficient route to extract polyphenols, reducing sugars and soluble lignin [46]. Apart from total yield of phenolic compounds, the research on the extraction of specific families of phenols from vine stems was also performed [47]. Solution plasma processing was found to improve the extraction of flavan-3-ols and flavonols, with less efficiency towards

stilbenes. For better performance, the addition of ethanol (50%) and the regulation of pH at 2.5 were necessary. The combined plasma-ethanol-pH treatment resulted in an increase of extractability of flavan-3-ols by 21% and of flavonols by 12% as compared to the standard hydro-ethanol extraction.

A similar combinatorial approach was applied for the treatment of rapeseed straw or rapeseed hulls, except that the solution plasma processing was combined with the chemical treatment by alkali or organosolv [48-50]. The main focus was set on the delignification, which was found to be improved for the plasma-alkali treatment. Nevertheless, the interaction with the plasma resulted in partial degradation of cellulose in straw. The solution plasma processing of rapeseed hulls with the subsequent chemical treatment by NaOH resulted in an enhancement of the yield of acid insoluble residues by 8% and in a higher enzymatic digestibility.

Bamboo shoot shells, rice straw, corn cob and stalk were treated by in-liquid pulsed DC discharge (up to 800 V and 1.3 A) with glycerol/water used as a medium and H_2SO_4 used as catalyst [51, 52]. Liquefaction of the biomass was studied in dependence on the biomass-to-liquid ratio, the catalyst concentration and the treatment time. Under optimized conditions, the liquefaction yield of 97% for bamboo shoot shells, 91% for corn cob, 87% for corn stalk and 72% for rice straw were achieved. The treatment also produced a large amount of a gaseous mixture consisting of H_2 (96.1-98.1%), CO (1.3-2.4 %) and $CH_4/C_2H_6/C_2H_4$ (0.6-1.2%).

Grass and leaves of some plants were also subjected to solution plasma treatment. *Eichhornia crassipes* (water hyacinth) was treated by in-liquid DC discharge (300-500 V) to valorize this free-floating aquatic plant, which otherwise causes serious problems in navigation and other human activities in Asia and South Africa [53]. Improved delignification and an increased sugar yield were reported as compared to the untreated weed.

The earlier-mentioned in-liquid pulsed arc discharge (up to 40 kV and 10 kA per pulse) was applied to leaves of *Stevia rebaudiana Bertoni*, a lignocellulosic source of non-caloric sweeteners [54-56]. It was confirmed that such treatment may help to increase the extraction yield of steviol glycosides (stevioside and rebaudioside A) which are sweet-tasting, yet calorie-free, compounds possessing a strong sweetening power. A concomitant recovery of antioxidant polyphenols (flavonoids, chlorophylls, and carotenoids) was proven as well.

A modified DBD in contact with air-bubbled solution (16.4 kV, 21.2 kHz, pulse width 100 ms, duty cycle 0.05-0.45) was used to treat *Miscanthus x giganteus* which is a perennial grass with exceptionally rich carbohydrate content [57]. *Miscanthus x giganteus* is cultivated primarily in Europe as well as in North and South America, and its very high biomass yield makes this grass a commercially relevant energy crop that is used for combustion in power plants. It is also considered to be attractive in biorefinery, provided that the lignocellulosic mass is delignified, cellulose is then hydrolyzed to monosaccharides and these simple sugars are further converted to bioethanol. The DBD resulted in the generation of O_3, OH radicals and other ROS and RNS which were efficiently transferred to the liquid phase, interacted with the lignocellulose biomass and led to the 0.5% release of acid-soluble lignin and in 26% release of sugars.

Table 1
Solution plasma treatment of plants
Таблица 1. **Плазменно-растворная обработка растений**

Material / discharge type	Main results	Reference
birch and willow shoots, barley straw in H_2O in-liquid pulsed arc discharge	enhanced extraction of reducing sugars, increased milk productivity of cattle fed with the plasma-processed fodder	[42]
vine shoots in H_2O in-liquid pulsed arc discharge	enhanced extraction of polyphenols (by 72%), reducing sugars (by 34%) and soluble lignin (by 104%).	[43-47]
rapeseed straw and hulls in H_2O or NaOH in-liquid pulsed arc discharge	delignification of rapeseed straw with enhanced extraction of reducing sugars and soluble lignin.	[48-50]
bamboo shoot shells, corn cob, corn stalk, rice straw in glycerol, PEG and H_2SO_4 in-liquid pulsed discharge	liquefaction of lignocellulose, release of H_2, CO, CH_4, C_2H_6 and C_2H_4	[51, 52]
Eichhornia crassipes (water hyacinth) in $FeCl_3$ in-liquid DC discharge	crystallinity decreases, lignin content decreases to 18%, sugar yield increases by 126.5%	[53]
Stevia rebaudiana Bertoni leaves in H_2O in-liquid pulsed arc discharge	enhanced extraction of high-added compounds (stevioside, rebaudioside A) and antioxidants	[54-56]
Miscanthus x giganteus grass air DBD in contact with air-bubbled solution	increased amount of acid soluble lignin and sugars	[57]

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Algae

So far, only a limited number of studies have been performed on solution plasma processing of algae, although the mass market production of algae-based materials has seen a huge growth since the mid-20th century. These aquatic plants serve as a commercially valuable source for food industry, cosmetics, biofuel refinery, as fertilizers, etc. Intracellular components of algae are rich with polysaccharides and other valuable compounds that may be beneficial in biomedicine as antioxidant and anti-inflammatory agents.

The extraction of intracellular components from microalgae *Nannochloropsis sp.* was carried out by various methods including in-liquid pulsed arc discharge (up to 40 kV and 10 kA) [58] (Table 2). The plasma treatment was shown to lead to the disruption of the microalgae cells and to the release of ionic components, mainly water-soluble low molar-mass species. The extraction of water-soluble proteins was also reached but to a much lesser extent. On the other hand, the extraction of light-absorbing pigments (chlorophylls and carotenoids) was not effective.

Table 2

Solution plasma treatment of algae
Таблица 2. **Плазменно-растворная обработка водорослей**

Material / discharge type	Main results	Reference
Nannochloropsis sp. in H_2O in-liquid pulsed arc discharge	cell disruption, selective extraction of soluble ionic components, small molar mass organic compounds and proteins	[58]
Scenedesmus in tap H_2O in-liquid plasma jet with Ar/O_2	effective destruction of the algae cells	[59]
Gracilaria Lemaneiformis in H_2O in-liquid pulsed discharge	extraction of valuable polysaccharides consisting of galactose, glucose, mannose, xylose, arabinose and fucose	[60]

Another example can be found in a recent work dealing with the treatment of water suspensions of green algae *Scenedesmus* by the gases effluent from the submerged AC plasma jet [59]. The plasma treatment was accompanied by a decrease of pH and led to cell lysis (87%). The largest part of remaining cells (80%) was not viable.

Water suspensions of ground *Gracilaria Lemaneiformis* macroalgae were treated either by circulating or continuous in-liquid pulsed discharge (9-15 kV, up to 300 A, pulse repetition frequency 3 Hz) to extract polysaccharides [60]. It was shown that the circulating

arrangement allowed for the highest polysaccharide yield. The extracted polysaccharides were shown to consist mainly of galactose and glucose with smaller contribution from mannose, xylose, arabinose and fucose.

Plant-derived by-products

Industrial processing of plants is accompanied by the production of significant amounts of secondary products and wastes that may further serve as sources of useful compounds. Solution plasma processing can prove to be a green route to the extraction of high added-value compounds or to controllable modification of plant-derived by-products.

Sawdust

Sawdust is a lignocellulosic biomass generated as a by-product of woodworking industry. In-liquid pulsed arc discharge (up to 40 kV, 45 kA) was applied to treat beach-wood sawdust as well as spruce needles [61] (Table 3). The discharge produced compressional waves that triggered mechanical destruction of lignocellulose with the formation of finer particles. The mechanical destruction also led to the release of reducing saccharides and easily hydrolyzed polysaccharides, their amount increasing with the number of the discharge pulses.

Pine-wood sawdust was treated in a NaOH solution activated by the above-liquid DC (15 and 30 mA) glow discharge with a liquid cathode [62]. An increase of porosity of the sawdust was detected which was accompanied by the amorphization of cellulose as well as by chemical transformations including the removal of hydrophobic compounds and an increase of the concentration of OH-based functional groups. The treated sawdust showed an improved sorption of Zn^{2+} ions from aqueous solutions. The method was suggested to be feasible for the production of low-cost sorbents for wastewater treatment.

Solution plasma processing was also applied to sawdust as part of a biorefinery procedure with the purpose of sawdust liquefaction and the production of biofuels. In-liquid bi-polar pulsed DC discharge (up to 800 V and 1.3 A) was used to treat pine-wood sawdust suspensions in glycerol and polyethylene glycols with the addition of H_2SO_4 as a catalyst [52, 63]. The concentration of the reagents was optimized to reach the liquefaction yield of 99.48%. The degradation of lignin was confirmed and the liquid products were enriched with carboxyls, ketones, aldehydes, esters, ethers and phenols.

Bast fibers

Bast fibers are obtained from the regions of plant stems adjacent to a wooden core. Various types of bast fibers (jute, hemp, flax, kenaf, ramie, etc.) are now gaining popularity in the global consumer market.

Until recently, these fibers were used only for the production of technical textiles, rope products, and heat-insulating materials for construction. However, many countries turn to using this resource actively with the purpose of obtaining fundamentally new types of materials. Fabrics and knitwear developed from modified bast fibers are distinguished by their unique properties: smoothness, low electrification, breathability, hygroscopicity, high UV absorbance, and ensure comfort of clothing due to effective heat and moisture exchange.

Being derived from plants, bast fibers also consist mainly of cellulose (62-70%), hemicellulose (12-17%) and lignin (2-12%) [64-67], which affects drastically the mechanical robustness of the fibers. The amount of the constituents in the fibers of different nature differs slightly with the exception of cotton which is characterized by a very high concentration of cellulose (82-93%), lower concentration of hemicellulose (5-6%) and the absence of lignin. For the application purposes, lignin should be removed from the fibers to improve their mechanical performance.

Hemp, flax and jute fibers were treated by plasma processing of NaOH solution and compared to the conventional NaOH treatment without plasma [17, 34, 68-70] (Table 3). Above- and in-liquid DC discharge as well as in-liquid diaphragm discharge was investigated. It was found that only an insignificant part of the degradation products passed into the solution after the plasma treatment. Nevertheless, such preliminary plasma activation significantly increased the delignification efficiency during the subsequent alkaline treatment. The delignification degree reached 68% for flax, 64% for hemp and 39% for jute in such two-stage treatment. It was concluded that the solution plasma treatment initiated the destruction of lignin and contributed to its subsequent dissolution and more efficient removal from the fibers. Boiling in an alkaline solution without plasma pre-activation did not provide comparable results. Thus, the two-stage processing scheme was preferable, with the first stage involving the preliminary activation of the destruction of lignin by plasma treatment of the fibers in an alkaline medium followed by the second stage involving the chemical treatment of the fiber with sodium hydroxide solution.

The experiments also showed that it was not necessary to use strong alkaline solutions as media for the plasma treatment. Positive results were obtained when using a solution of sodium carbonate or tap water. For example, if the plasma treatment in tap water was followed by conventional boiling in an alkaline solution, it allowed reducing the lignin content in flax fiber by 53% and in hemp by 55%. However, the delignification degree was only 23% when modifying jute fibers. In this case, it was necessary to use both an alkaline medium during the plasma processing and special delignification compounds at the boiling stage for effective removal of lignin.

Later, similar in-liquid DC plasma treatment was applied to flax fibers but acidic HNO_3 medium was used instead of NaOH [71]. The acidic treatment was found to be more effective in terms of delignification as compared to the alkaline treatment. It was also confirmed that the two-stage process (solution plasma treatment with subsequent acidic boiling) provides the best results.

Strong interest in solution plasma processing of bast fibers is further evidenced by a number of patents granted in the past years covering the utilization of in-liquid pulsed arc discharge [72-74] and, allegedly less energetic, in-liquid pulsed discharge of an unspecified type [75], claiming that such processing can be used as part of a complex fiber treatment and may lead to efficient delignification with the retention of the original length and diameter of the bast fibers.

Nutshells

Nutshells are another example of abundant wastes produced in agriculture after the nutmeat has been removed. The estimations show that, for instance, the production of dry cocoa beans corresponds to the tenfold production of cocoa shells. Taking into account the huge annual production of nuts, it is not surprising that various methods have been considered to reduce the amount of by-products discarded as wastes. Solution plasma processing was suggested as one of the possible approaches. The main efforts were put onto the valorization of nutshell residues as dye or heavy metal ion sorbents with the purpose of producing low-cost replacement to activated carbon. *Jatropha curcas*, cocoa, walnut and peanut shell powders were treated by different types of discharges including above-liquid gliding arc discharge [28, 29], DBD in ultra-fine water mist [76] and in-liquid pulsed arc discharge [77]. Regardless of the method used, all reports agree on the enhancement of the efficiency and sorption capacity of the plasma-treated shell biomass for the extraction of industrial textile dyes (efficiency up to 94.6%, sorption capacity up to 65.6 mg/g) and removal of Cu^{2+} (efficiency up to 98 %, sorption capacity up to 39.4 mg/g) from aqueous solutions. Furthermore, high efficiency of flavonoid (high added-value polyphenolic antioxidants) extraction from peanut shells has also been reported [77].

Seeds, fruit peels, press-cake and pomace

It is worth noting that the extraction of high added-value bioactive compounds from agricultural and food industry by-products is by itself a stand-alone

task. In-liquid pulsed arc discharge (up to 40 kV, 10 kA) was extensively used to valorize seeds [78-83], fruit peels [84-89], press-cake and pomace [49, 83, 90-96]. Similar to the treatment of plants described above, this type of the discharge released substantial mechanical energy into the biomass-containing liquid, thus inducing damage to cell membranes and leading to an enhanced release of bioactive compounds.

The first researches were focused on the improvement of the extraction of oil from linseeds and sesame seeds [78, 81]. A multi-stage process was developed in which solution plasma processing was used to eliminate the mucilage before an enzymatic treatment and for the treatment of solid residues, both without the loss of oil.

The following works dealt with the solution plasma-assisted extraction of valuable bioactive compounds from seeds (grape-, papaya-, rapeseeds), peels (papaya, mango, orange, pomegranate peels, olive kernels and rapeseed hulls), pomace and press-cake (grape pomace, flaxseed, rapeseed and sesame cakes, sugar beet pulp). Despite being exceptionally diverse, all these agricultural products, by-products and wastes are rich in polyphenols (flavonoids, phenolic acids, stilbenes, lignans), a family of compounds that have strong health benefits as antioxidants. Polyphenols can be also used as dyes, tanning agents or as precursors in chemical synthesis. It was shown that in-liquid pulsed arc discharge can result in an increase of the total polyphenol yield. For example, a 7-fold increase was reported for grape pomace [93]. Recovering of other valuable compounds such as proteins, carbohydrates and isothiocyanates was also documented. On the other hand, it was admitted that such treatment may produce undesirable chemical products and free radicals as well.

A similar approach was applied to extract polyphenols from spent coffee grounds by their treatment with in-liquid pulsed arc discharge (8-17 kV, pulse repetition frequency 3 Hz) [97]. The method allowed reaching higher polyphenol yield with lower energy consumption as compared to conventional solvent extraction.

Table 3

Solution plasma treatment of plant-derived by-products
Таблица 3. **Плазменно-растворная обработка побочных продуктов растительного происхождения**

Material / discharge type	Main results	Reference
1	2	3
Sawdust		
beech-wood sawdust and spruce needles in H_2O in-liquid bi-polar pulsed arc discharge	physical destruction of the materials, enhanced post-treatment hydrolysis with the formation of saccharides and polysaccharides	[61]
pine-wood sawdust in NaOH above-liquid DC discharge with liquid cathode	amorphization of cellulose, increase of the OH concentration, increase of porosity, enhanced sorption of Zn^{2+}	[62]
pine-wood sawdust in glycerol, PEG, H_2SO_4 in-liquid bi-polar pulsed DC discharge	liquefaction of lignocellulose	[52, 63]
Bast fibers		
flax, hemp, jute in NaOH above- and in-liquid DC discharge and in-liquid diaphragm discharge	lignin removal (68% flax, 64% hemp, 39% jute), enhancement of water absorption ability by the fibers	[17, 34, 68-70]
flax in HNO_3 in-liquid AC discharge	the plasma treatment in acid is more efficient than that in alkali	[71]
flax, hemp, jute, nettle, kenaf in H_2O	removal of lignin with retention of the original length and diameter of the fibers	[72-75]
Nutshell		
Jatropha curcas or *Theobroma cocoa* shell husk in H_2O above-liquid gliding arc discharge	biosorbents with enhanced removal of industrial textile cationic and anionic dyes	[28, 29]
walnut shell powder in H_2O mist DBD in ultra-fine water mist	enhanced carboxylation of powder and 98% removal efficiency of Cu^{2+}	[76]
peanut shell in H_2O + C_2H_5OH in-liquid co-axial pulsed arc discharge	enhanced extraction of flavonoids	[77]

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Seeds		
1	2	3
linseeds in H_2O in-liquid pulsed arc discharge	separation of mucilage from linseeds without loss of oil	[78]
grape seeds in H_2O + C_2H_5OH in-liquid pulsed arc discharge	the discharge damages cell membranes and accelerates the extraction of polyphenols	[79, 80]
sesame seeds in H_2O in-liquid pulsed arc discharge	the oil yield increases by 22.4%	[81]
papaya seeds and rapeseeds in H_2O in-liquid pulsed arc discharge	extraction of proteins, phenolic compounds, carbohydrates and isothiocyanates; extracts are unstable	[82, 83]
Pomace and press-cake		
papaya, mango, orange and pomegranate peels and olive kernels in H_2O in-liquid pulsed arc discharge and diaphragm discharge	enhanced extraction efficiency to recover high added-value compounds (reducing sugars, polyphenols, pectin)	[84-89]
grape pomace in H_2O; flaxseed, rapeseed and sesame cakes, sugar beet pulp in H_2O + C_2H_5OH, in-liquid pulsed arc discharge	higher yield of extracted solutes and of polyphenols which becomes enhanced with shock waves exceeding 100 bars and/or with the addition of ethanol	[49, 83, 90-96]
spent coffee grounds in H_2O + C_2H_5OH in-liquid pulsed arc discharge	high polyphenol yield and lower energy consumption as compared to solvent extraction	[97]

Plant-derived polymers

As discussed earlier, plant-derived lignocellulose biomass consists mainly of cellulose, hemicellulose and lignin. Of all the nature-derived polymers, cellulose is the first and lignin is the second (together with chitin, see below) most abundantly found material in nature [98]. These natural polymers have high industrial importance per se; nevertheless, further improvement/modification of their properties can be needed for specific applications and this is where solution plasma processing can play a significant role.

Cellulose and hemicellulose

Cellulose is a linear polymer consisting of $\beta(1{\rightarrow}4)$-linked D-glucose units (Fig. 3). The availability of oxygen and hydrogen atoms in the structure results in the formation of multiple hydrogen bonds between the neighbouring chains, holding them tightly together and producing a highly crystalline microfibrillar motif. The highly ordered structure is responsible for the mechanical robustness of cellulose as well as for its insolubility in water and most organic solvents. Nevertheless, the crystalline microfibrils of naturally-occurring cellulose are typically intermediated by less ordered amorphous regions with weaker bonding (hemicellulose) which are more prone to a mechanical or chemical attack. In contrast to solely glucose-based cellulose, hemicellulose consists of multiple and randomly distributed sugar monomers that include (but are not limited to) glucose, xylose, mannose and galactose. The use of elevated temperature and pressures as well as acidic media makes it possible to remove the amorphous hemicellulose regions and isolate the crystalline cellulose microfibrils. The resultant product is commonly known as microfibrillated/nanocellulose (mc-cellulose) reflecting the fact that the fibrils have high aspect ratio with the length and width ranging in micro- and nanoscale, respectively. A more intensive treatment may produce smaller cellulose particles of < 1 μm size which are known as cellulose nanocrystals (nc-cellulose). If the treatment conditions are chosen to be extremely harsh, cleavage of the glycosidic bonds may lead to the conversion of cellulose to a mixture of mono- and polysaccharides.

Solution plasma processing was suggested to replace the conventional pathways of cellulose treatment to achieve better compliance with the modern demands of sustainability. The first reports appeared in 1970s and were related to the use of electrohydraulic effect of in-liquid pulsed arc discharges [99] (Table 4). Although diverse plasma-based approaches have been used since then, the results of such treatment bear similar physical and chemical features.

I) Cellulose undergoes amorphization. The overall destructive influence of plasma results in a decrease of crystallinity and makes the structure more accessible for further treatment [100, 101].

II) Solution plasma processing of all kinds leads to the fragmentation of macromolecular chains of cellulose accompanied by a decrease of the average molar mass, which is manifested typically via a decrease of viscosity of cellulose suspensions [61, 102, 103].

III) Chemical as well as mechanical scission of the glucosidic linkages may lead to the release of lower molar mass water-soluble compounds, oligo- and mono-saccharides being the main components thereof.

IV) Cellulose becomes partly oxidized and carboxyls are the species frequently detected as a result

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of such oxidation [102-108]. Reportedly, it is the formation of carboxyls that facilitates the proton attack on the glycosidic bond resulting in an enhanced scission of these bonds and in depolymerization of cellulose [103].

In particular, a 7.6% yield of the soluble mass was reported for DC discharge with ionic liquid used as a cathode (1000 Pa, 500 V, 40 mA) [109]. About half of the soluble mass was reported to belong to unspecified reducing sugars.

In-liquid bi-polar pulsed discharge (1.6 kV, pulse width 3 μs, pulse repetition frequency 15-30 kHz) resulted in up to 42% conversion of cellulose to monosaccharides (maltose, glucose, xylose and mannose) [100]. The use of Fe electrodes was shown to be beneficial for the increase of total reducing sugar yield. It was suggested that Fe ions catalyze the decomposition of plasma-generated H_2O_2 leading to an enhanced generation of OH radicals, which participate in the destruction of the glycosidic bonds. It was also shown that such solution plasma processing did not lead to the further degradation of the synthesized monosaccharaides. The same type of the discharge, but used with the presence of a Ru/C catalyst, allowed for the conversion of cellulose to sugar alcohols (sorbitol and mannitol) [110].

The treatment of microcrystalline cellulose by the modified DBD in contact with air-bubbled solution (10.6 kV, 29 kHz, pulse width 100 ms, duty cycle 0.10-0.45) resulted in an increase of solubility of cellulose to 70% and led to a more efficient subsequent enzymatic hydrolysis with 51% conversion of cellulose to glucose [101].

Another variation of the solution plasma processing was suggested for the hydrolysis of hemicellulose to monosaccharides [111]. In the first step, distilled water was treated by above-liquid DBD (80 W) and such plasma-activated water was used as a medium for the hemicellulose treatment. Acidification of water upon the plasma activation was reported, with pH decreasing to 2.8. As hemicellulose is much more vulnerable to acidic hydrolysis as compared to cellulose, such pH value was sufficient for its complete conversion to glucose, xylose and galactose with the yield of 38.67%, 9.28% and 3.09%, respectively.

Apart from the synthesis of low molar mass carbohydrates, solution plasma processing of cellulose was also considered as a route to fuel gas production [112, 113]. Suspensions of cellulose were treated by in-liquid RF discharge (27.12 MHz, 150 W power) combined with ultrasonication. Gas chromatography was used to detect and quantify the release of H_2 (52-68%) with the smaller contribution from CO, CO_2, CH_4, C_2H_4 and C_2H_2. A manifold increase of the total fuel gas yield was observed when the cellulose concentration in the suspension was raised to 50 wt. %. Introduction of NaOH and ultrasonication to the suspensions was also beneficial for the enhancement of the gas yield.

Solution plasma processing of cellulose was also suggested for the synthesis of novel composite materials with advanced functionalities. For example, in-liquid DC discharge (6000 V, 43 mA) was ignited in the solution of hydroxyethylcellulose and Na_2SO_4 to initiate the post-treatment grafting of copolymer of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid [114]. The resultant copolymer/cellulose hydrogels exhibited high absorption capacity for heavy metal ions (Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}) and were suggested for use as super-absorbents. A similar approach was used to graft the copolymer of acrylic acid and N-isopropyl acrylamide onto solution plasma-treated hemicellulose [115, 116]. In addition to the absorption capacitance for Pb^{2+}, Cd^{2+} and Zn^{2+} ions, those hydrogels exhibited temperature/pH dual sensitivity.

A resembling, yet modified strategy was used to deposit plasma polymerized coating of polyacrylic acid onto cotton fabrics and paper (cellulose-rich materials) with subsequent grafting of cationic fluorosurfactant [31]. DBD was maintained in He atmosphere (20 kV, 100 kHz, 30 W) above the water solution of acrylic acid into which the cellulosic samples were submerged. In this manner, cellulose was coated by thin film of polyacrylic acid and fluorosurfactant was subsequently grafted to render a surface with hydrophilic/oleophobic properties. The material was presumed to be relevant as a membrane for oil/water separation.

An opposite functionality of a deliberate release of metal ions into aqueous solutions was realized by solution plasma processing with the purpose of developing antibacterial cellulose-based composite materials. In-liquid unipolar pulsed discharge (800 V, 30 kHz, pulse width 2 μs) was ignited in the cellulose solutions with the addition of $AgNO_3$ [117]. The discharge resulted in the reduction of Ag^+ ions, with the formation of 5-30 nm Ag nanoparticles (NPs). These were embedded into 3D microporous cellulose scaffolds by lyophilization. The Ag/cellulose scaffolds showed bactericidal activity against various pathogens including *E. coli, P. aeruginosa, V. parahaemolyticus, S. aureus,* and *B. cereus.*

In another work, bacterial cellulose hydrogel-like pellicle was saturated with $Zn(NO_3)_2$ solution and then introduced into a solution plasma processing reactor with methanol used as a liquid medium [118]. In-liquid bi-polar pulsed discharge (1.44 kV, pulse width 2 μs, pulse repetition frequency 15 Hz) was run to induce the formation of ZnO NPs within the cellulose matrix. The ability of a Zn^{2+} ion release made this composite material bactericidal against *E. coli* and *S. aureus.*

Solution plasma processing of cellulose and hemicellulose
Таблица 4. **Плазменно-растворная обработка целлюлозы и гемицеллюлозы**

Material / discharge type	Main results	Reference
cellulose in H_2O in-liquid pulsed arc discharge	enhanced accessibility of cellulose to subsequent acetylation in acetic acid	[99]
methylhydroxyethylcellulose in H_2O in-liquid bi-polar pulsed discharge	decrease of the molar mass	[61]
mc-cellulose in H_2SO_4 in-liquid bi-polar pulsed discharge	up to 42% conversion of cellulose to monosaccharides (maltose, glucose, xylose and mannose)	[100]
mc-cellulose in pH 3, 7 and 9 buffers air DBD in contact with air bubbled solution	best results obtained for pH = 3 (solubility increase to 70% and conversion to glucose increases to 51%)	[101]
mc-cellulose in H_2O or dilute H_2SO_4 DC discharge with liquid cathode	cellulose carboxylation, conversion to nanocellulose	[102, 103]
mc-cellulose in H_2O DC discharge with liquid cathode or diaphragm discharge	enhanced mobility of cellulose particles in solution due to increased concentration of polar groups on the surface	[104]
cotton yarn in NaH_2PO_4 in-liquid diaphragm AC discharge	increase in the wicking rate of cotton yarn	[105]
mc-cellulose in H_2O or H_2O_2 in-liquid Ar plasma jet	carboxylation (enhanced by H_2O_2), bactericidal effect against *E. coli*	[106]
mc-cellulose in H_2O in-liquid Ar (+ O_2, N_2) RF plasma jet + ultra-sonication	defibrillation of cellulose, functionalization with O- or N-bearing moieties	[107, 108]
cellulose in ionic liquid DC discharge with liquid cathode, low pressure	7.6% of cellulose decomposes (3.9% to sugars)	[109]
mc-cellulose in H_2O with Ru/C catalyst in-liquid bi-polar pulsed discharge	conversion of cellulose to sugar alcohols (sorbitol and mannitol)	[110]
hemicellulose + plasma-treated H_2O air DBD on H_2O	complete hydrolyzation of hemicellulose with the formation of monosaccharides (glucose, xylose and galactose)	[111]
cellulose in H_2O or NaOH in-liquid RF discharge + ultrasonication	generation of H_2 and other low-grade flammable gases	[112, 113]
hydroxyethyl cellulose in Na_2SO_4 in-liquid DC discharge	discharge-initiated grafting of acrylate polymers with enhanced absorbance of heavy metal ions from aqueous solutions	[114]
cotton and paper in acrylic acid/H_2O above-liquid DBD in He	coatings of polyacrylic acid with hydrophilic-oleophobic properties	[31]
reed hemicellulose in Na_2SO_4 in-liquid N_2-bubbled DC discharge	re-usable temperature/pH-sensitive hydrogels are synthesized with high adsorption capacity to Pb^{2+}, Cd^{2+} and Zn^{2+}	[115, 116]
cellulose in $AgNO_3$ in-liquid unipolar pulsed discharge	3D scaffolds of cellulose/Ag NPs (5-30 nm) biocomposites, bactericidal effect against *E. coli, P. aeruginosa, V. parahaemolyticus, S. aureus,* and *B. cereus*	[117]
Zn^{2+}-loaded bacterial cellulose in CH_3OH in-liquid bi-polar pulsed discharge	ZnO/cellulose nanocomposite bactericidal effect against *E. coli* and *S. aureus*	[118]

Lignin

Lignin together with hemicellulose mediates the structural pattern of cellulose microfibrils in the walls of plant cells and determines the overall mechanical rigidity of the structure. Lignin is an aromatic polymer with a complex structure characterized by the absence of a uniform type of bonds between the phenylpropane monomer units (Fig. 3). The structure of lignin was often considered to be of three-dimensional character, although recent studies argue this statement and suggest the structure to be linear [98]. The main bonds in lignin are ether bonds in the α and β positions of the propane chain, ether bonds between aromatic

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units (aryl-O-aryl), carbon-carbon bonds between aromatic units and alkyl radicals (for example, –CH₃), and carbon-carbon bonds such as aryl-aryl, aryl-alkyl, or alkyl-alkyl.

The composition and structure of lignin depends on the type of plant. Differences in the sets of monomer units and in the ratios of functional groups in the composition of macromolecules can be found even in the lignin of plants belonging to the same type.

The difficulty of the removal of lignin from plants is given both by its structure and the presence of carbon-carbon bonds, which are extremely resistant to the action of various reagents. The resistance of lignin to hydrolysis determines the choice of sufficiently rigid processing parameters in wet chemical methods. For example, strongly alkaline or acidic solutions in combination with specially selected redox reagents are conventionally used [98].

The huge annual production of paper is accompanied by the production of huge amounts of lignin which is extracted as a by-product of the process of delignification of lignocellulose. The majority of lignin is further used as fuel for combustion in power plants. However, the predominantly aromatic structure of lignin makes it attractive as a low-cost source for the synthesis of lower molar mass high added-value derivatives.

Presumably, the first liquid phase plasma treatment of lignin was reported in 1999 [119] (Table 5). In-liquid Ar-bubbled DC discharge was ignited in suspensions of lignin powder in $SiCl_4$. The treatment showed that polydimethylsiloxane moieties can be firmly attached to the lignin particles.

Later, in-liquid DC discharge (0.2-1.0 A) was applied to the solutions of lignin and isoeugenol (a model lignin compound) in NaOH to induce damage to the lignin structure [120, 121]. A three-fold increase of the solubility of lignin after the plasma processing proved that the structural destruction was effective. Chemical analysis confirmed that aromatic and unsaturated aliphatic structures were partly decomposed.

Anisole is another compound that bears the structural motif of lignin and can be used to analyze the influence of solution plasma processing on the chemical transformations of the aromatic structure. Pulsed DBD (9 kV, 20 kHz, pulse width 50 ns, pulse repetition frequency 20 kHz) was run in He/anisole mist with or without the presence of metal/metal oxide catalysts [122, 123]. An up to 81% anisole conversion was achieved for the catalytically assisted process. The main products of the conversion were identified as 4-methylanisole, phenol and benzene that were produced via transalkylation, demethylation and hydrogenolysis of anisole, respectively.

Mist of lignin solution in NaOH was treated by pulsed corona discharge (20 kV, 400 A, pulse width 100 ns, pulse repetition frequency 100-840 Hz) in air or in O_2-enriched synthetic air [124]. The formation of vanillin and, occasionally, syringaldehyde was confirmed. It should be mentioned that vanillin was also synthesized by solution plasma processing of lignin solutions using the above-liquid DC pulsed discharge (10-18 kV) in Ar or air [125].

Described earlier for cellulose treatment, in-liquid RF discharge (27.12 MHz, 200 W power) was used in combination with ultrasonication to treat the solutions of lignin in methanol [126]. Generation of gaseous products was set in the focus of the research. Similar to the cellulose case, the production of H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_2 was confirmed. Furthermore, the decomposition of lignin resulted in the production of low molar mass aromatic compounds including benzene, toluene and phenol.

Table 5

Solution plasma processing of lignin
Таблица 5. **Плазменно-растворная обработка лигнина**

Material / discharge type	Main results	Reference
lignin in $SiCl_4$ in-liquid Ar-bubbled DC discharge	grafting of lignin with polydimethylsiloxane moieties	[119]
lignin and isoeugenol in NaOH in-liquid DC discharge	3-fold increase of lignin solubility, destruction of aromatic structures	[120, 121]
anisole (model lignin compound) catalytic ns- pulsed DBD in He/anisole mist	anisole demethylation, transalkylation and hydrogenolysis	[122, 123]
lignin in NaOH pulsed corona discharge on showered solution (air or N_2/O_2)	decomposition of lignin with the formation of vanillin and syringaldehyde	[124]
lignin in H_2O above-liquid DC pulsed discharge (Ar, air)	synthesis of high added-value compounds (vanillin)	[125]
lignin in CH_3OH in-liquid RF discharge (27.12 MHz) + ultrasonication	generation of gases (H_2, CO, CH_4, C_2H_2, CO_2, C_2H_4), benzene, toluene, phenol	[126]

Other plant-derived mono- and polysaccharides

Besides the research on solution plasma processing of cellulose/hemicellulose and lignin, other plant-derived polymers have also attracted attention in the last years, although the number of the as yet published works is not very high. The research on starch can be considered as a logical spin-off of the experiments with cellulose, as both polymers are composed of the same *D*-glucose monomer units (Fig. 3 and Fig. 4). In starch, the monomer units are bound by α-glucosidic linkages as opposed to β-linkages characteristic for cellulose. Starch is extensively used in industry for the conversion into sugars by acidic and/or enzymatic hydrolysis, or by malting with subsequent fermentation of sugars to ethanol.
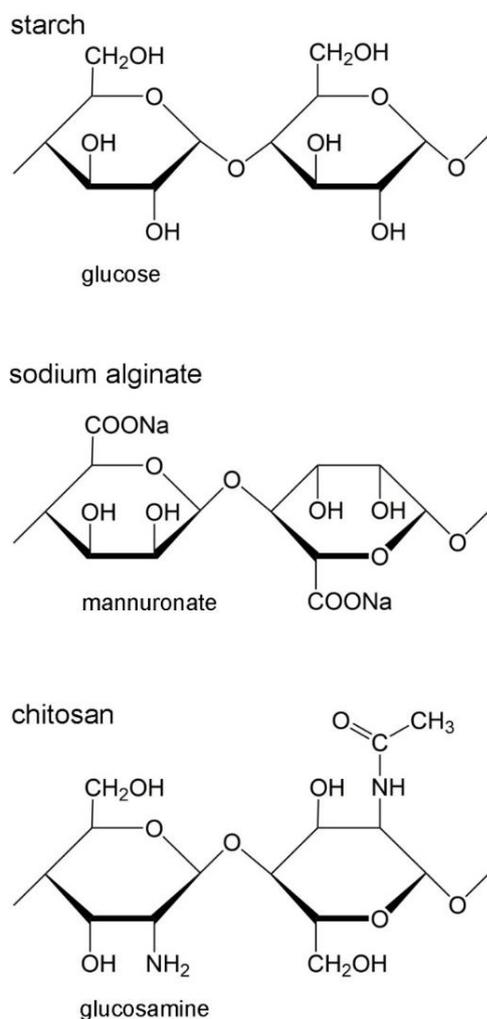

Fig. 4. Structure of several natural polymers subjected to solution plasma processing

Рис. 4. Структура нескольких природных полимеров, подвергнутых плазменно-растворной обработке

Solution plasma processing was suggested as a non-conventional acid/enzyme-free approach for conversion of starch into sugars. Above-liquid DBD [127, 128], plasma jet [129] as well as in-liquid pulsed discharge [130] were used to treat aqueous suspensions of starch (Table 6). The common trend can be found in a fast decrease of pH of the solution upon the plasma treatment of all kinds. Conversion to sugars has also been reported either as an increase of the concentration of unspecified mono- and disaccharides [127], total reducing sugars [130] or, more specifically, as an increase of the concentration of glucose [128, 130].

An original approach was also developed in which starch was used as a diagnostic reagent to study the transport and reactivity of ROS supplied to liquid from atmospheric pressure He/O$_2$ plasma jet [32, 33]. Aqueous solutions of starch and potassium iodide (KI) were prepared and treated by the plasma jet. The research took advantage of the well-known phenomenon of formation of I$_3^-$ ions by the action of ROS and their subsequent complexation with starch. The iodide-starch complex absorbs light specifically at $\lambda = 600$ and 450 nm, and straightforward optical diagnostics can therefore be used to monitor spatial distribution of ROS in the liquid.

Although glucose is a monomer, it is worth mentioning for the sake of completeness that glucose solutions were also treated by plasma either with the purpose of generating H$_2$ [131] (the reader may compare this research with the earlier cited works of the same authors on cellulose [112, 113] and lignin [126]) or to use glucose (fructose and sucrose as well) as inducers for the synthesis of porous MnO$_2$ from KMnO$_4$ solutions [132]. Furthermore, honeys (natural mixtures of glucose, fructose and other minor components) activated by atmospheric pressure plasma jet were suggested to be used for acute wound healing [133, 134]. Although no decisive evidence was obtained about the favorable effect of such treatment on the acceleration of wound healing, the research highlights the scientific interest emerging in the medicine-oriented community to find non-conventional solutions of therapeutic issues.

Another group of works focused on solution plasma processing of sodium alginate. Sodium alginate is a sodium salt of alginic acid, a linear polysaccharide present abundantly in and extracted commercially from cell walls of marine brown algae [135] (Fig. 4). The main benefits of sodium alginate are related to its biocompatibility and ease of gelation. These properties make this natural polymer attractive for use in food industry, pharmaceuticals and cosmetics. In medicine, sodium alginate is investigated for its potential in tissue engineering, wound healing and drug delivery.

In-liquid bi-polar pulsed discharge (1.1 kV, 2 μs pulse width, pulse repetition frequency 15 kHz) was ignited in aqueous solutions of sodium alginate with or

without the addition of $HAuCl_4$ [136-138]. Depolymerization of sodium alginate was observed via a decrease of the viscosity of the solutions. The resultant alginates were characterized by narrow distributions of molar masses [136]. The addition of chloroauric acid resulted in reduction of gold ions, with the formation of Au NPs of non-uniform shape. The NP size was controllable by the treatment time and it ranged from 46 to 7 nm [137]. It was also shown that the use of gold-containing electrolytes is not necessary for the synthesis of Au NPs provided that gold electrodes are used for the ignition of plasma [138]. Gold atoms were supplied into the solution via the erosion of the electrodes upon the influence of the discharge. The process led to the nucleation of spherical NPs that grew to the size of 3-5 nm. Anionic alginate effectively passivated the NPs which resulted in the production of colloidal solutions very stable even at prolonged storage time.

A similar approach utilized in-liquid uni-polar discharge (800 V, 30 kHz) to treat sodium alginate solution with the addition of $AgNO_3$ [139]. Spherical Ag NPs were synthesized with the mean size changing from 5 to 40 nm. Microporous composite 3D scaffolds were produced by lyophilization after the plasma treatment and they showed antibacterial activity against nine human pathogens including gram-negative bacteria (*Escherichia coli, Vibrio vulnificus, V. parahaemolyticus, Pseudomonas stutzeri, P. aeruginosa*), gram-positive bacteria (*Staphylococcus aureus, Bacillus cereus*), yeast (*Candida albicans*), and a fungus (*Aspergillus parasiticus*).

Two quite recent papers addressed the investigation of solution plasma processing of polysaccharides extracted from *Auricularia auricular*, a fungus extensively used in South Asia as a food and medicine supplement [140, 141]. In-liquid air-bubbled pulsed discharge (60 kV, 350 W, pulse width 40 ns, pulse repetition frequency 4.67 kHz) was ignited in the polysaccharide solution with or without the addition of H_2O_2. The research aimed at the conversion of the original polysaccharide into a mixture of lower molar mass polymers, as lighter polysaccharides of *Auricularia auricular* exhibit stronger antioxidant activity. A decrease of the solution viscosity with the treatment time evidenced the depolymerization of the precursor and the formation of lower molar mass fragments. Importantly, the plasma treatment did not change the main structural motif of the polysaccharide, which was confirmed by FTIR and NMR. An enhanced antioxidant activity of the plasma-treated *Auricularia auricular* polysaccharide was observed via a Fe ion-chelating effect.

Agarose gel was treated by above-liquid DBD in air (20 kV, 1 kHz, 0.3 W/cm^2) to model the penetration of ROS and RNS into open wound tissues [142]. Agarose is a linear polysaccharide that is obtained from red seaweed. It is used widely for electrophoretic separation of peptides, chromatographic purification of proteins and as a model of brain tissue. The penetration of plasma-generated H_2O_2 into the agarose gel resembled strongly the penetration of H_2O_2 into animal tissues. It was concluded that the gel can be used as a reliable model without the need to use live animals.

Table 6

Solution plasma processing of other plant-derived polysaccharides
***Таблица 6.** Плазменно-растворная обработка других растительных полисахаридов*

Material / discharge type	Main results	Reference
1	2	3
Starch		
starch in H_2O above-liquid air DBD	61% conversion of starch to mono- and disaccharides	[127]
starch in H_2O above-liquid He DBD	decrease of pH, conversion to glucose and acetic acid	[128]
starch in H_2O above-liquid air plasma jet	decrease of pH, decrease of relative crystallinity, increase of water-binding capacity and swelling volume	[129]
starch (cassava starch waste) in H_2SO_4 in-liquid bi-polar pulsed discharge	Enhanced yield of total reducing sugars (99.0%) and glucose (47.9 %) as compared to conventional acid hydrolysis	[130]
starch-agarose gel in H_2O above-liquid O_2/He plasma jet	KI-starch/agarose gel detects ROS supplied to and generated in H_2O by plasma jet	[32, 33]
glucose in H_2O in-liquid RF discharge (27.12 MHz) + ultrasonication	synthesis of H_2	[112, 131]
glucose, fructose or sucrose in $KMnO_4$ in-liquid bi-polar pulsed discharge	hierarchical nanoporous MnO_2 for cationic dye removal	[132]

1	2	3
honey solution in phosphate buffer saline above-liquid Ar AC plasma jet	positive supportive effect on acute wound healing	[133, 134]
Sodium alginate		
sodium alginate in H_2O in-liquid bi-polar pulsed discharge with W electrodes	depolymerization of sodium alginate	[136]
sodium alginate in $HAuCl_4$ in-liquid bi-polar pulsed discharge with W electrodes	Au NPs with controllable shape and size are stabilized in alginate matrix	[137]
sodium alginate in H_2O in-liquid bi-polar pulsed discharge with Au electrodes	chemical-free synthesis of size-dependent spherical Au NPs stabilized in alginate matrix	[138]
alginate in $AgNO_3$ in-liquid uni-polar pulsed discharge with W electrodes	3D microporous scaffolds of alginate/Ag NPs (5-40 nm) biocomposites, bactericidal effect against 9 pathogens	[139]
other polysaccharides		
polysaccharide from fungi *Auricularia auricular* (AAP) + H_2O_2 in-liquid air-bubbled ns-pulsed AC discharge	degradation of AAP with narrowed molar mass distribution and with retention of its primary structure; higher antioxidant activity and metal chelating effects	[140, 141]
agarose gel in H_2O or PBS above-liquid μs-DBD in air	agarose gel may serve as a model for real tissue, DBD treatment allows controlling the acidity and the penetration depth of H_2O_2 into the gel	[142]

SOLUTION PLASMA PROCESSING OF ANIMAL-DERIVED POLYMER-BASED MATERIALS

Chitosan

Of all the animal-derived polymer-based materials, chitin and chitosan are noted for attracting the greatest scientific attention in the solution plasma polymerization community. Chitin is the main component of exoskeletons of crustaceans and insects, and of cell walls in fungi. Food industry produces huge amounts of shrimp- and crab-shell wastes that serve as a primary source for commercial chitin production.

Chitin has very close structural analogy to cellulose: it is a linear polymer consisting of glucose units in which one hydroxyl group is replaced by an acetyl amine group (Fig. 4). Similar to cellulose, such *N*-acetylated glucose units are linked via $\beta(1{\to}4)$-glycosidic bonds composing long macromolecular chains. Another common feature is that both polymers tend to self-organize to acquire a micro- and nanocrystalline fibrous structure. Strong inter- and intra-molecular hydrogen bonding provides the mechanical robustness and chemical stability to the fibrils.

Chitosan is a well-known derivative of chitin produced by the deacetylation of its *N*-acetyl groups, with the formation of primary amine groups. High chemical resistance of chitin requires the use of strong reagents to fulfil this conversion so that commercial procedures of the deacetylation involve the treatment of chitin in NaOH solutions at elevated temperatures. The resultant chitosan is characterized by a degree of deacetylation (DD, the ratio of glucosamine to *N*-acetyl-glucosamine groups) ranging from 60 to 100%. In contrast to cellulose, surprisingly little has been done with solution plasma-assisted chemical conversion of chitin. The community rather focused on the plasma modification of already-deacetylated chitosan, taking no notice of the chitin deacetylation issues themselves.

Chitosan is highly attractive for its biocompatibility and biodegradability. It has been used in agriculture and food industry for a long time, and in recent years it has been intensively investigated for potential use in biomedicine as wound dressing, bioadhesive or drug-delivery material. Solution plasma processing of chitosan was suggested as an alternative route to the controlled modification of its properties and the first papers appeared several years ago [143-145] (Table 7).

Close similarity to cellulose explains the fact that solution plasma processing of chitosan was performed in a manner close to the cellulose treatment, often by the same groups studying both polymers in parallel. The difference can be found in the aggregation state: chitosan can be dissolved in water, yielding colloidal solutions (especially in weakly acidic environment) whereas water-insoluble cellulose is treated in suspensions. The general trends observed for the solution plasma treatment of chitosan are also similar to

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cellulose and they involve: I) amorphization; II) depolymerization; III) formation of oligosaccharides and IV) partial oxidation.

I) Chitosan forms coatings if plasma-treated solutions are evaporated after the treatment. The degree of crystallinity is typically smaller as compared to the precursor chitosan [146-152]; however, at least one paper exists that reports on the formation of a more ordered structure with a higher degree of crystallinity after the plasma treatment [144].

II) Chitosan undergoes depolymerization leading to a decrease of the average molar mass, which typically manifests through a decrease of viscosity of chitosan solutions [145-159]. The formation of different fractions of chitooligosaccharides was confirmed [150-152, 155, 156] with the smallest oligomers reaching the degree of polymerization of 2-8 [147], although the complete conversion to glucosamine monomer units has never been reported as opposed to the synthesis of glucose monomer units from cellulose. It should be noted that one research reports on the production of both lower and higher molar mass chitosan as compared with the original polymer [30].

III) Depolymerization proceeds predominantly via the cleavage of the glucosidic bonds, which ensures a good retention of the original chemical structure [30, 145-159].

IV) Nevertheless, minor oxidation of the glucosamine units with the formation of carbonyl-based functionalities cannot be avoided [150, 153].

Chitosan-based materials are typically obtained by drying plasma-treated solutions. A limited number of papers dealt with direct deposition of chitosan films onto solid supports during the solution plasma processing [143, 153]. Above-liquid DC discharge with liquid cathode (673 V, 30 mA) was applied to treat chitosan solutions in which polypropylene foils were submerged [153]. The treatment led to bond cleavage in both chitosan macromolecules and polypropylene. As a result, chitooligosaccharides were coupled to the polypropylene surface by covalent linkages. The development of mechanical stress in the coatings was reported that resulted in specific structuring of the film surface.

In the last years, the research moved to incorporating foreign (and often nanostructured) material to chitosan matrices, thus adding new functionalities to the final product. Metals are the most frequent add-ons that are purposed to enhance the antibacterial properties of chitosan. Similar to the processing of cellulose, attempts were performed to treat chitosan solutions with the addition of metal salts; however, certain peculiarities have been met. The addition of $Ca(NO_3)_2$ and $NH_4H_2PO_4$ to chitosan solutions and the treatment of these mixtures by in-liquid unipolar pulsed discharge (400 V, duty cycle 0.3, pulse repetition frequency 100 Hz) resulted in the deposition of composite coatings on titanium surface [143]. The coatings consisted of chitosan with embedded solid particles of inorganic salts containing calcium and phosphorus.

The addition of $CuSO_4$ was attempted with either in-liquid bi-polar pulsed discharge (1.44 kV, 2 µs pulse width, 15 kHz) [149] or with in-liquid air-bubbled pulsed AC discharge (60 kV, 350 W, pulse width 40 ns, pulse repetition frequency 4.67 kHz) [159]. In both cases, reduction of Cu ions to metal copper has never been reached and the formation of chitosan-Cu(II) complexes was rather reported. Ion complexation with chitosan without the synthesis of metal NPs was also reported for $Zn(NO_3)_2$ and $FeCl_3$ [149], and this contrasts markedly with the mentioned earlier work by the same authors on the solution plasma processing of $Zn(NO_3)_2$/cellulose mixtures showing the formation of ZnO NPs [118].

Controversial results were obtained also for $AgNO_3$. The formation of chitosan-Ag(I) complex was reported in [149] whereas reduction of silver ions with the production of Ag NPs was achieved using in-liquid unipolar pulsed discharge in $AgNO_3$/chitosan solution [155]. Similar to the coatings from $AgNO_3$/cellulose [117] and $AgNO_3$/sodium alginate [139] solutions, Ag NPs/chitosan scaffolds exhibited antimicrobial activity against gram-positive and gram-negative bacteria and fungi. Chitosan coating itself showed an antibacterial effect, although it was less prominent as compared to Ag NP-loaded coatings.

It can be assumed that it is the presence of primary amines that is responsible for the substantial deviations of plasma processing of chitosan/inorganic salt solutions from the processing of the same salts mixed with non-amine natural polymers. It can be also concluded that even the plasma processing of similar chitosan/salt mixtures may lead to different results depending on experimental conditions, and that our understanding of the concomitant phenomena is far from being complete.

Another example of the use of solution plasma processing for the production of chitosan-based composite materials can be found in [160, 161] where in-liquid glow discharge (630 V, 52 mA) was ignited in the mixtures of chitosan, 2-acrylamido-2-methyl-1-propanesulfonic acid and acrylamide. Porous chitosan-based hydrogels were produced that exhibited sorption capacity for cationic dyes.

Finally, chitosan/graphene oxide composite membranes were synthesized by treating distilled water with above-liquid DBD in air (125 W) with the subsequent use of thus-acidified water (plasma acid by the notation of the authors) as a solvent for chitosan and graphene oxide [162]. The membranes were produced by drying the solutions and, as a consequence, graphene oxide was reported to be dispersed uniformly in the chitosan matrix. Potential applications of these membranes in biomedicine or textile industry were suggested.

Other animal-derived polymers

A number of works have been published on solution plasma processing of collagen and it's irreversibly hydrolyzed form – gelatin. Collagen is the most abundantly found protein in mammals and it is used in numerous biomedical applications including tissue engineering, wound healing, bone grafting and others. Water-insoluble collagen can be converted to water-soluble gelatin by the treatment with acidic or alkaline solutions as well as by enzymatic hydrolysis.

In-liquid unipolar pulsed discharge (450 V, 0.6 A, duty cycle 0.1, pulse width 5 μs, pulse repetition frequency 20 kHz) was applied to blood-filled collagen sheets that mimicked clots of chronic total occlusions [163]. Radicals generated in the liquid phase were found to break the amide III bonds of collagen, leading to its denaturation and dissolution. The use of collagen as a proxy model of blood clots was validated.

Solution plasma-treated collagen was also tested for wound healing. Nebulized collagen solution was supplied to a corona plasma jet in He (115 V, 148 kHz, duty cycle 0.44) and the plasma-activated aerosol was directed onto chronic wounds [164]. It was shown that collagen retained its structure after the treatment. Moreover, the collagen deposits facilitated wound closure and angiogenesis as compared to untreated wounds or to wounds treated with the plasma without the collagen solution. It was concluded that such plasma spraying can be effective for delivery of other natural polymers in the form of therapeutic coatings.

Collagen solutions were treated by above-liquid microsecond (20 kV, pulse repetition rate 1 kHz, 1.1 W) and nanosecond (24 kV, pulse repetition rate 1 kHz with power of 9.7 W, and pulse repetition rate 0.1 kHz with power of 0.8 W) pulsed DBD in air and they were compared with the likewise treated liquid Matrigel, a commercially available extracellular matrix consisting of a gelatinous mixture of proteins [165]. Both *in vitro* and *in vivo* studies of chondrogenesis and bone formation showed that the microsecond-DBD treated gels increased the invading cell number, enhanced cartilage differentiation and facilitated bone formation. The treatment with the nanosecond-DBD induced the opposite effects. It was concluded that the experimental conditions may be tuned to either accelerate or inhibit chondrogenesis and endochondral ossification.

Gelatin solutions were treated by in-liquid bipolar pulsed discharge (1.6 kV, 2 μs pulse width, 15 kHz) [166]. In contrast to cellulose and chitosan, the plasma processing resulted in an increase of the viscosity of the gelatin solutions which was further enhanced by the addition of ethanol. The effect was ascribed to the formation of free radicals in the solution that triggered an enhanced cross-linking in gelatin gels. The enhanced cross-linking was also confirmed by the shift in the position of the IR amide I and amide II bands as well as by the gel strength tests. It was also emphasized that accurate control of the solution temperature is very important because gelatin exhibits thermo-responsive properties. The above-described cross-linking was achieved at 22 °C whereas depolymerization of gelatin occurred at 40 °C leading to a decrease of the solution viscosity [167].

Collagen and gelatin were used as capping agents for the synthesis of either Au NPs from HAuCl₄ by in-liquid Ar RF plasma jet (2 kV, 10 MHz) [168] or Sn NPs by in-liquid pulsed discharge with Sn electrodes (10 kV, 50 Hz, duty cycle 0.25, 15 W) [169]. Although collagen and gelatin were used in these studies simply as auxiliary substances to stabilize the colloidal NP solutions, the papers can serve as examples of solution plasma synthesis of collagen/gelatin-modified NPs.

The deliberate synthesis of Ag NPs/gelatin composite materials was accomplished by the treatment of AgNO₃/gelatin solutions by in-liquid bi-polar pulsed discharge (1.6 kV, 20 kHz, pulse width 2 μs) [170, 171]. Microporous 3D scaffolds were prepared after the treatment by lyophilization. It was shown that spherical 10-15 nm sized Ag NPs were successfully embedded into the gelatin matrix. The biocomposites exhibited antifungal effect against *C. albicans* and *A. parasiticus* as well as antibacterial effect against *E. coli* and *S. aureus*.

Another study focused on solution plasma processing of heparin, a linear glucosaminoglycan consisting of variably sulphated 1→4-linked disaccharide units [172]. Heparin is widely used as a blood anticoagulant, although unwanted side effects limit its long-term administration. In-liquid bi-polar pulsed discharge (250 V, pulse width 5 μs, pulse repetition frequency 30 kHz) was applied to the heparin sodium salt with the purpose of synthesizing low molecular weight heparin (LMWH). LMWH is known to be superior to unfractionated heparin in terms of reduced side effects

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and antithrombotic activity. Indeed, the plasma treatment resulted in a continuous decrease of the heparin molecular weight with the treatment time. The main channel of the treatment involved the attack of the OH radicals onto the glycosidic linkages leading to depolymerization of heparin, yet with the retention of its chemical structure and characteristics.

Table 7

Solution plasma treatment of animal-derived polymers
Таблица 7. **Плазменно-растворная обработка полимеров животного происхождения**

Material / discharge type	Main results	Reference
1	2	3
Chitosan		
chitosan in CH_3COOH, $Ca(NO_3)_2$, $NH_4H_2PO_4$ (DD = 90%) in-liquid unipolar pulsed discharge	Ca and P enriched chitosan coatings on Ti substrates, poor adhesion	[143]
chitosan powder in Na_2SO_4 (DD = 91%) in-liquid DC discharge	enhanced dye absorption from aqueous solutions	[144]
chitosan in CH_3COOH/C_2H_5OH in-liquid unipolar pulsed discharge	decrease of chitosan molar mass	[145]
chitosan in CH_3COOH (DD = 85%, M_V = 190 – 310 kDa) above-liquid DBD in He	the chemical structure remains intact, the formation of fragments of either lower or higher molar mass	[30]
chitosan in CH_3COOH (DD = 90 and 95 %, M_V = 550, 210 and 130 kDa) + $AgNO_3$, $Zn(NO_3)_2$, $CuSO_4$, or $FeCl_3$ in-liquid bi-polar pulsed discharge	chitosan depolymerization with the formation of fragments of lower molar mass, loss of crystallinity, synthesis of chitosan/metal ion complexes	[146-149]
chitosan in carboxylic acids + H_2O_2, $K_2S_2O_8$, $NaNO_2$ (DD > 90 %, M_V = 480 kDa) in-liquid bi-polar pulsed discharge	chitosan depolymerization with the formation of water-soluble chitooligosaccharides, inhibitory effect towards cancer cells	[150-152]
chitosan in CH_3COOH + $AgNO_3$ (DD = 85 %, M_V = 100 – 300 kDa) in-liquid unipolar pulsed discharge	chitosan depolymerization with the formation of fragments with M = 46 kDa, synthesis of fibrous 3D scaffolds with 2.5-27.6 nm sized Ag NPs, antibacterial activity against various pathogens	[155, 156]
chitosan in CH_3COOH + H_2O_2 (+ $CuSO_4$) (DD > 90%, M_V = 1138 kDa) in-liquid air-bubbled ns-pulsed AC discharge	gas bubbling and H_2O_2 accelerate the chitosan depolymerization, the main chemical structure remains intact, chitosan/Cu(II) complex with enhanced antioxidant activity is produced	[157-159]
chitosan in CH_3COOH (DD = 82%, M_V = 195 kDa) above-liquid DC discharge with liquid cathode	chitosan depolymerization with the formation of fragments of lower molar mass, chitosan attachment to polypropylene foils	[153, 154]
chitosan in PEG, MBA and acrylic acid (DD = 85%) in-liquid glow discharge	synthesis of chitosan/polyethylene glycol/polyacrylic acid composite absorbent for Pb^{2+} and Cd^{2+} removal from aqueous solutions with successive regeneration	[160, 161]
chitosan in plasma-treated H_2O + graphene oxide (DD > 85%) above-liquid DBD in air	chitosan and graphene oxide dissolve in plasma-treated water, composite membranes can be produced	[162]
Other animal-derived polysaccharides		
collagen (blood-filled), equine blood clots in saline in-liquid unipolar pulsed discharge	denaturation of collagen leads to the clot dissolution without tissue damage	[163]
collagen in CH_3COOH (neubulized aerosol) corona plasma jet in He	The plasma-treated collagen reduces inflammation and enhances chronic wound healing	[164]

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1	2	3
collagen and matrigel (extracellular matrix protein mixture) above-liquid μs- and ns-DBD in air	μs-DBD enhances cell numbers, cartilage differentiation and increases bone formation in mice, ns-DBD has the inverse effect.	[165]
gelatin in H_2O + C_2H_5OH in-liquid bi-polar pulsed discharge	enhanced cross-linking of gelatin gels and decrease of free amino acid content at 22 °C; gelatin depolymerization at 40 °C	[166, 167]
collagen in HCl + $HAuCl_4$ in-liquid Ar-bubbled RF plasma jet	synthesis of collagen-coated 11 nm-sized Au NPs	[168]
gelatin in H_2O in-liquid pulsed discharge with Sn electrodes	synthesis of gelatin-coated 20-40 nm Sn NPs	[169]
gelatin in $AgNO_3$ in-liquid bi-polar pulsed discharge	3D microporous scaffolds of gelatin/Ag NPs (10-15 nm) biocomposites, antifungal effect against *C. albicans* and *A. parasiticus*, antibacterial effect against *E. coli* and *S. aureus*	[170, 171]
heparin in H_2O in-liquid bi-polar pulsed discharge	Decrease of the heparin molar mass without synthesis of by-products, no change in the main characteristics of heparin	[172]

CONCLUSIONS

The results accumulated so far show the effectiveness of the plasma-solution approach for the modification of natural polymer-based materials. This is especially true if the solution plasma processing is used as part of more complex modification protocols. Ultrasonication, acidic, alkaline, organosolv or enzymatic delignification of plants (birch, willow, bamboo and vine shoots; barley, rice and rapeseed straw; perennial grasses), plant-derived by-products and wastes (sawdust, bast fibers and nutshells) were shown to be significantly accelerated by the contribution from the solution plasma treatment. The approach seems to be feasible for the valorization of agricultural wastes, for the production of biofuels as well as for the synthesis of high added-value chemical compounds. A distinct direction of the solution plasma processing of both plant- and animal-derived natural polymers lies towards the synthesis of novel composite materials (metal/polymer, polymer/polymer) with controlled crystallinity, porosity, distribution of molar masses and chemical composition. If achieved, the precise control over these parameters will allow for the use of solution plasma-treated natural materials as low-cost and sustainable heavy metal and dye absorbers, antibacterial scaffolds, materials for wound healing and tissue engineering, and in other applications.

Nevertheless, insufficient fundamental knowledge of the physical and chemical processes occurring in plasma-treated solutions hinders this emerging approach from being widely accepted. Further development of these methods is required and it is associated with the development of new or modernization of existing technological hardware as well as with the utilization of new diagnostic and theoretical approaches.

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