

# Scientific and Technical Solutions to the Problem of Utilization of Waste from Plant- and Mineral-Based Industries

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**Abstract**—High potentialities offered by plant- and mineral-based waste as promising raw materials for various industrial processes were overviewed.

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Industrial processing of natural resources results in conversion to the end product of only insignificant proportion (in selected cases, 1.5–2%) of raw materials, whose major part undergoes various modifications and is run to waste, most of which is stored in specially allotted sites. Waste storage leads to alienation and disturbance of the fertility of large land areas whose reclamation does not provide timely reintroduction into commercial activities [1].

As regards solid industrial waste products, they come primarily from ore mining and smelting, as well as fuel and energy sectors; further contributors include chemical and building industries and processing facilities in other, in particular, agricultural, sectors.

In this context, it should be noted that, since 1970s, much popularity has been enjoyed by the approach to addressing eco-economic problems based on clean production concept. The basic principles of this approach, considered to be the most reasonable both ecologically and economically, can be formulated as follows: “The commonsense, precautionary response to burgeoning pollution problems is to seek to prevent pollution before it happens. Where it is already occurring, the aim should be to eliminate the source of the problem rather than attack symptoms through often expensive “end of pipe” methods such as filters, scrubbers, treatment plants, and incineration.” [2]. An ever increasing number of business operators is beginning to realize that pollution is an evidence of inefficient activities by the companies they manage, and waste is the lost resource and, hence, a lost benefit.

Waste processing allows offloading the lands allotted for waste dumping sites and reducing the environmental pollution. A best possible use should be made of waste materials in production processes so that they could be brought back into natural cycles of matter. Those views, expressed as early as by V.I. Vernadskii in his time, should underlay the approach to solving industrial and domestic waste problem, which relies on their use rather than disposal.

When discussing the waste processing issue, it should be recognized that there exists a great diversity of waste products. They can be classified in terms of a number of characteristics such as, e.g., origin (plant-based, inorganic), hazard (extremely hazardous, severely hazardous, moderately hazardous, low-hazardous, non-toxic), composition (carbon-, silicon-, phosphorus-containing, other), etc.

As to plant-based waste materials, the major options for their minimization include the use in production of building materials and constructions, as well as composting, combustion for heat energy generation, and preparation of fodder products [3–7].

Waste products from wood and agricultural products processing represent valuable lignin-carbohydrate raw materials which, in certain instances, could replace high-quality wood, thereby contributing to natural resources conservation. Those possibilities were strongly corroborated by the results of a study [8] dedicated to pyrolysis-based methods of processing of difficultly utilizable waste from chemical forest complex. In that work, waste materials were sub-

divided into several groups (bark, sawdust, hydrolytic lignin; liginosulfonates, black liquor; activated sludge, lignin slurry), depending on their suitability for processing, and subjected to combined pyrolysis-activation, oxidative pyrolysis, and energetically self-sufficient pyrolysis.

The first method consists in injection of water vapor directly into the pyrolysis zone where chopped wood materials is placed. The carbon matrix gets activated via destruction of its most reactive surface segments, so that the inner pores, until then closed, become accessible for gases and liquids. A combination of pyrolysis with activation allows improving the active carbon yield by 15–20% relative to individual pyrolysis and activation procedures [9]. Oxidative pyrolysis is most suited for processing of mineralized waste, e.g., sewage sludge [10]. The energetically self-sufficient pyrolysis method is suitable for processing of lumpy wood waste products [11]. This procedure can be used for combined steam-gas power generation in which process additional heat energy is generated. It was found [8] that, at  $\leq 58\%$  moisture content of raw material, the heat generated from gas burning exceeds that required for achieving the desired thermal characteristics of reactors. Based on this technology, installations with the capacity of 300 and 500 tons of coal per annum were developed and put into operation.

The carbonized materials resulted from pyrolysis act as efficient adsorbents in wastewater treatment to remove organic impurities at pulp and paper mills and hydrolysis plants, as well as for treatment of ammonia-containing gases [12, 13].

Softwood logging residue can replace traditionally used birch wood in production of clearing active carbons [14, 15].

Sorbents (in particular, active carbons) are in great demand for various industrial applications, which circumstance necessitates the search for ways of their preparation not only from wood and wood processing waste but also from other plant-based materials, in particular, agricultural and agricultural product processing waste.

Preparation of sorbents from technical lignins (lignosulfonates, hydrolytic lignins) and their carbonizates has been the focus of much research. Its outcome was a great diversity of suggested solutions to this problem, in particular: a technique for preparation of ion-exchange resins from lignosulfonates [16, 17], hydrolytic lignin, and activated concentrate of spent liquor [18]; a method for sulfonation of hydrolytic lignin with sulfuric acid into a product similar to sulfonated

carbon [19]; a method for chemical modification of hydrolytic lignin slurry into biodegradable phytosorbents suitable for elimination of toxicants from human body and disinfection of environmental objects [20]; and other techniques for chemical and thermal modification of hydrolytic lignins into adsorbents intended for diversified purposes [21–31].

Another raw material for active carbon preparation was found in cotton plant stalk waste [32]. Examination of thermal decomposition of this waste material showed that pyrolysis, which is carried out at  $\sim 300^\circ\text{C}$  after the drying stage ( $20\text{--}100^\circ\text{C}$ ), involves reactions of formation of free radicals and depolymerization, and carbonyl- and carboxy-containing compounds are also formed, which processes give rise to various organics and carbon residue. In the final stage, calcination of carbon residue, the organics and resins are removed, and noncondensable gases are evolved.

Using the mathematical design of experiment, the pyrolysis conditions for cotton plant stalk were optimized: heating rate  $2.5^\circ\text{C min}^{-1}$ , end temperature of the process  $375^\circ\text{C}$ , time of exposure of the raw materials at the end temperature 45 min, and inert gas flow rate  $0.31\text{ dm}^3\text{ min}^{-1}\text{ cm}^{-2}$ . Under these conditions, the respective yields of noncondensable gases ( $\text{CO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2$ , and minor amount of  $\text{CO}_2$ ), distillate (a watered mixture of acetic acid, acetone, methyl acetate, methyl propionate, etc.), and lumped charcoal were 43.5, 18.5, and 36.2%, respectively [33]. The lumped charcoal characteristics were as follows: bulk weight  $255\text{ g dm}^{-3}$ , moisture content 5.05%, ash content 7.5%, sorption capacity toward benzene, iodine, and Methylene Blue  $0.120\text{ cm}^3\text{ g}^{-1}$ , 34.8%, and  $14.06\text{ mg g}^{-1}$ , respectively; total pore volume (water)  $1.2\text{ cm}^3\text{ g}^{-1}$ ; micro-, meso-, and macropore volume 0.11, 0.16, and  $0.93\text{ cm}^3\text{ g}^{-1}$ , respectively; and specific surface area of mesopores  $81.19\text{ m}^2\text{ g}^{-1}$ . Steam activation under optimal conditions (temperature  $760^\circ\text{C}$ , steam flow rate  $18.7\text{ dm}^3\text{ min}^{-1}\text{ cm}^{-2}$ , and treatment time 40 min, as follows from the mathematical design of experiment) gave carbon with the following characteristics: bulk weight  $240\text{ g dm}^{-3}$ ; relative humidity 2.87%, ash content 15.2%, sorption capacity toward benzene, iodine, and Methylene Blue  $0.176\text{ cm}^3\text{ g}^{-1}$ , 56.8% and  $124.8\text{ mg g}^{-1}$ , respectively; total pore volume (water)  $1.4\text{ cm}^3\text{ g}^{-1}$ ; specific volume of micro-, meso-, and macropores 0.18, 0.24, and  $0.98\text{ cm}^3\text{ g}^{-1}$ , respectively; and specific surface area of mesopores  $377.17\text{ m}^2\text{ g}^{-1}$ .

Based on the results of those studies, a process flowsheet and the design of a setup for the production

of active carbons from cotton plant stalks (with the capacity of 300 tons of carbon per annum) were developed [34].

Another practically important direction of plant-based waste processing consists in preparation of sorbents, in particular, those from nut shells and fruit stones.

Some countries use coconut and hazelnut shell, as well as olive pits, for preparation of active carbons [24], which display good sorption properties and high strength responsible for their regenerability and reusability.

Also, a procedure for preparation of modified active carbons from peach kernel shell was proposed [35]. It consists in mechanical (tribochemical) activation of fruit kernels, followed by chemical treatment (mainly with zinc chloride or sulfuric, hydrochloric, or phosphoric acids) and thermal activation (in a carbon dioxide atmosphere) [36]. The resulting sorbents showed activity in removal of sulfur dioxide from gas emissions and of active chlorine from aqueous solutions. Both those processes were efficiently (99%) implemented in the developed [37] process schemes which employ a mass-exchange apparatus [38] filled with activated peach kernel shell.

Carbonization of walnut shells, apricot kernels, and grape seeds [39–41] gives carbon sorbents which display good sorption capacity with respect to heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , etc.). This is due to a high specific surface area and developed pore structure of these sorbents, as well as to the presence of surface carboxy, carbonyl, and phenolic groups, whose hydrogen ion can be substituted by a metal ion to form slightly dissociated compounds, chelate surface complexes [42, 43]. Acid activation of the resulting materials, as well as their surface modification by immobilization of yeast cells [44–46], cause enhancement of the major adsorptive properties (specific surface area, sorption capacity with respect to iodine, Methylene Blue, etc.) and the ability to sorb heavy metals.

For prospective outlook on the above-discussed research activities, see [47, 48].

Along with carbonization, chemical modification of plant-based waste products was examined [49–52]. Specifically, it was shown that treatment of apricot kernel and walnut shell with alkali, as well as with mineral and organic acids, is advantageous over heat treatment in terms of the enhancing effect these procedure exert on selectivity of the resulting sorbents with respect to heavy metal ions.

Carbon sorbents can be produced not only from various organic waste products but also from the ballast, as well as from waste generated by solid fuel burning, coal extraction, and coke fines combustion [53, 54]. Though not equal to commercial active carbons in sorption capacity [55], the resulting materials offer substantial economic benefits in terms of low cost and availability of the raw materials and suitability as a fuel. They show good performance in wastewater and industrial gaseous emission treatment and soil cleanup, in particular, in selective treatment of aqueous runoffs to remove zinc ions [53] and in cleaning up soils contaminated with pesticides and other xenobiotics [56].

Considerable application in wastewater and waste gas treatment domain is also enjoyed by inorganic sorbents prepared from mineralized waste containing aluminosilicates or calcium silicate components. With these sorbents, the sorption processes follow the heterogeneous ion exchange, electron exchange, and molecular sorption mechanisms. For example, ferrochromium slag, ash from heat and power generation plants, and aluminum production sludge are suitable for sorption treatment of lead-zinc production wastewater [57–59]. Also, the possibility of preparation of sorption-active materials, silicate slag sorbents based on magnesia-iron dry granulation slag, was analyzed [60]. Acid etching and alkali etching procedures applied to phosphorous slags in predetermined sequence yield sorbents that can be used for removal of hydrogen chloride from air [61].

It must be stressed that phosphorus-containing slag processing is an issue of much importance for Kazakhstan with its world's largest plants for production of phosphorus and its compounds. The existing technologies mostly focus on production of building materials from electrothermophosphorous slags [62–64] and allow underutilization only, which necessitates the search for new sound technical solutions.

Bases on phosphorus production slags and mill tailings of polymetallic and rare-metal ores and ashes, a technology was developed for production of new aluminosilicate materials and porous fillers [65]. The application of this technology allows expanding the raw material base for ceramic industry, saving fuel and raw materials, reducing the energy intensity of the manufacturing process, and improving the technical characteristics of the resulting materials.

Waste generated by electrothermal production of phosphorus is suitable for preparation of sorbents [66–

70] which show fairly good performance in water treatment to remove various pollutants, as well as of supports for catalysts used in oxidative dimerization of propylene, copper-slag catalysts for cyclohexanol dehydrogenation, platinum catalysts used in *n*-heptane conversion, and cobalt-molybdenum- and nickel-molybdenum-slag catalysts for hydrodesulfurization of oil fractions, which are equal in activity and selectivity to the known commercial analogs.

Some other silicate waste materials are also suitable as supports for catalysts and as catalysts and sorbents. For example, magnesia-iron silicate granulated slag was used for preparation of slag silicate support for nickel, cobalt, and copper catalysts applied in pyrocondensate hydrogenation [71]. Metallurgical slags can serve as raw materials for preparation of catalysts for deep oxidation of organics [72] or as supports for catalysts in treatment of process gases to remove acetylene compounds [73].

Both carbon-containing and silicate waste products were tested as fillers for rubber articles. In particular, electrothermophosphorous slags are suitable as fillers of isoprene- or diprene-based rubber mixtures [74]. Phosphorus production waste can be used as filler both individually and in combination with commercial technical carbon or with technical carbon and carbon white, in the ratio of 5–20:45–20 and 2.5:45:2.5 (in parts), respectively.

The strength of rubbers filled with technical carbon can be improved by adding to the rubber mixture of coarsely dispersed slag containing silicon, calcium, phosphorus, and iron oxides [75].

It was shown [76] that dispersed waste from tuff production can replace chalk in rubber industry applications. With tuff-based filler, which is four times cheaper than chalk, modification of existing equipment and technological process is avoided; the physico-mechanical characteristics of the finished products are identical to those of standard (chalk-filled) ones.

Solid waste from production of propylene polymerization catalyst (the 30–50- $\mu$ m fraction) can replace zinc white, kaolin, chalk, and partly carbon white in manufacturing some types of shoe rubbers [77]. Replacement of traditional inorganic fillers by these materials leads to improved abrasion resistance of rubber, all other characteristics being identical to those of control vulcanisates.

The above discussion showed that there exist real possibilities for plant- and mineral-based waste to be

used in various production processes. The major arguments in favor of organizing large-scale waste processing include relative cheapness of the resulting materials and prospects for substitution of imported ones, as well as improved environmental conditions. Materials prepared from nonconventional feedstock are often identical in characteristics and thus competitive with commercial analogs.

However, the concept of preparation of inexpensive materials from industrial waste has not been properly implemented as yet. This is due mainly to the fact that production of any material, even of that from waste, needs arranging a special manufacturing process whose implementation, in turn, needs a careful technical and economic consideration.

At the same time, the problem of utilization of waste from production activities is still topical and, moreover, sharply aggravated under the existing circumstances, which sends scientists, technologists, engineers, and economists in the search for options to solve this problem.

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