

# 農業工学研究所技報

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# Utilization of Agricultural by-product-based Carbons

Wayne E. MARSHALL\* and SHINOGI Yoshiyuki\*\*

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## I Introduction

Activated carbon is the most widely used adsorbent material in the world. For example, in the United States and Japan, a major use is the removal of taste and odor from drinking water. It is manufactured in two forms, powdered and granular, with the granular form being the more prevalent (Activated Carbon Markets, 1994). Activated carbon can be manufactured from virtually any material that has a reasonable elemental carbon content. Commercially, activated carbon is usually produced from bituminous or lignite coal in the United States. In Japan, where coal is scarce, activated carbons are produced from imported coal, coconut shells and domestic wooden trash. However, in Japan, carbonization of rice husks, sugarcane bagasse, municipal sludge and animal manure have been proposed (Wartelle and Marshall, 2001). Moreover, production of carbon from these source materials (feedstocks) may prove to be an excellent optional technology for disposing and/or recycling of these plant and animal wastes. Coal has a relatively high elemental carbon content compared to other source materials for carbon production, and when converted to a carbon, the yields are about 45-47% of the original mass of the source material.

Other feedstocks for the commercial production of activated carbon in the United States include coconut shells, wood and peat (Bansal, et al., 1988). These feedstocks have a lower elemental carbon content than coal and thus activated carbon yields are in the range of 10-20% (Bansal, et al., 1988). Of the "other" feeds-tocks, coconut shells have the advantage of being a renewable resource where supplies are available on a nearly continuous basis. Nutshells, other than coconut shells have also been successfully converted to activated carbon and have been shown to have desirable physical, chemical and adsorption properties (Balci, et al., 1994, Ferro-García, et al., 1988, Gergova, et al., 1992, Gergova, et al., 1994, Heschel and Klose, 1995, Rivera-Utrilla and Ferro-García, 1987).

The Southern Regional Research Center (SRRC) laboratory at, New Orleans, LA, USA has been instrumental in developing nutshell-based carbons with excellent adsorptive properties toward metal ions, such as copper ion ( $Cu^{2+}$ ) (Johns, et al., 1999, Toles, et al., 1997, 1998, 1999, Toles, et al., 2000, Toles and Marshall, 2002). While many of these studies have reported developing good quality carbons for the adsorption of metal ions and organic compounds, the technology for carbon production and the carbons themselves have been, to date, simply confined to the laboratory. At the National Institute for Rural Engineering (NIRE) in Tsukuba, Japan, studies have been initiated on the development of manufacturing technologies and the utilization of pyrolyzed feedstock such as rice husk, straw and municipal sludge for use in soil amendment applications (Wartelle and Marshall, 2001). Activated carbons made from nutshells, other

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than those made from coconut shells and agricultural by-products have not been adopted, thus far, for commercial use.

The objectives of this paper are twofold. First, the paper provides a blueprint for activities that are required to interest the private sector in technology transfer of new carbon technologies and new carbon products. Second, the paper reviews developments in activated carbon technology produced at the SRRC that has led to the production of phosphoric acid-activated nutshell carbons with excellent metal ion adsorption. The technology could be developed on a large scale to interest the business sector, both in the United States and Japan, in adopting this technology for commercial purposes.

## II Requirements for Private Sector Interest

*Criteria for acceptance.* In order for nutshell-based carbons, other than coconut shell carbons, to be accepted as commercial products, preferably all three of the following criteria must be met: (a) nutshell-based carbons must be equivalent to commercial carbons in meeting certain basic specifications of surface area, bulk density and attrition, (b) nutshell-based carbons must be produced using a lower source material cost than commercial carbons, and (c) there must be available markets for the nutshell-based carbons. In other words, niche markets should be available to take advantage of the carbon's unique physical, chemical or adsorptive properties.

Based on these three criteria, are nutshells currently available, combined with new or current carbon manufacturing technologies, to produce a better and less costly carbon than existing commercial carbons? We believe that the answer to this question is "yes" and the reason for this answer will be based on research conducted at the SRRC over the last several years to develop a nutshell-based carbon that is a leader in metal ion adsorption. A description of this research is given under *Development of metal ion-adsorbing carbon*.

The use of nutshells combined with phosphoric acid activation process utilizing concurrent air oxidation can provide a better metal ion adsorbing carbon that may be less costly to sell than many granular activated carbons currently on the market.

*Currently available resources- feedstock cost and availability.* Of the commercially used feedstocks for granular activated carbon production, bituminous and lignite coals are the most prevalent in terms of availability, at least in the United States, and cost between \$70-120 (8,300-14,200 Yen) per metric ton in the US. In many other countries, coal may be scarce or unavailable. The same availability problem could be said for coconut shells and peat, and in some less common instances, for wood as well. Therefore, many countries must rely on their agricultural base to provide feedstock for activated carbon production. For example, in the United States, tree nuts, such as almond, pecan and English walnut, are the most plentiful of the nut crops. When shelled they create about 400,000 metric tons of shells that need to be disposed of based on the amount of nuts collected in the 2001 crop year (Anonymous, National Statistical Service, 2001). These shells are used as low value feed additives, animal bedding, mulch or as an abrasive in drilling mud. They are normally sold for about \$5-10 (600-1,200 Yen) per metric ton, much lower than the price of coal.

As currently manufactured in the United States, coal-based carbons require the use of a binder, either coal tar or wood tar. These binders cost about \$100-120 (12,000-14,200 Yen) per metric ton. In contrast to coal, no external binder is required with nutshells, as nature provides a lignocellulosic binder that keeps the nutshell intact. In addition to not requiring the extra expense of a binder, tree nutshells are renewable on a seasonal basis. This is in contrast to coal which is a non-renewable commodity.

*Currently available resources- environmental considerations.* In countries, such as the United States, Europe and Japan, environmental considerations related to activated carbon manufacture are important. Using the comparison between coal and nutshells as feedstock, the conversion of coal to carbon requires labor intensive mining to obtain the coal and the grinding and sieving of the coal in preparation for pyrolysis creates toxic dust. Pyrolysis of coal produces toxic, sulfur-containing gases that must be removed with costly air purification filters before the pyrolysis gases can be vented into the environment. Therefore, mining coal and then manufacturing activated carbon from this coal have the potential of creating human and environmental problems unless stringent safety precautions are in place at the production facility.

On the other hand, nutshells require no mining, milling of the shells generates non-toxic dust, and pyrolysis of the shells creates no sulfur-containing gases. Manufacturing of nutshell-based carbons solves an environmental problem of feedstock accumulation in already overburdened landfills.

*Cost to manufacture nutshell-based carbons.* In term of economics, we have estimated the manufacturing cost of phosphoric acid-activated, nutshell-based activated carbons and have calculated a value of \$2.45 (290Yen) /kg (Toles, et al., 2000). This calculation was based on constructing a turnkey production facility with a nutshell input of about 14,000 kg per day and a daily activated carbon output of about 5,000 kg. The estimate assumes that 90% of the phosphoric acid can be reclaimed during the carbon washing step, concentrated and reused once. The cost estimate also includes the addition of a water treatment unit to reduce the phosphate concentration in the wash water to acceptable levels for municipal sewage treatment. However, not included in this cost estimate is the manufacturer's profit and distribution and return on working capital.

In contrast, the cost to manufacture a typical coal-based carbon is not available because companies consider this information proprietary and do not want competitors to know their manufacturing cost and profit structure. However, the cost to purchase carbon in bulk (large lot) quantity is readily available and can vary greatly depending on the intended use. Bulk prices can range from about \$1.10-4.40(130-520 Yen)/kg, with prices for lesser amounts of product being much higher. However, these carbons generally have poor metal ion adsorbing capabilities (Johns, et al., 1998, 1999). By contrast, the best commercial metal ion adsorbing carbon on the market is a product of the Calgon Carbon Corp. (Pittsburgh, PA, USA) and is called Minotaur. The cost of purchasing Minotaur is \$22.00(2,603 Yen)/kg.

### III Activated Carbon Technology developed at the SRRC

*Granular activated carbon.* At the SRRC, granular activated carbon has been produced from nutshells. Granular carbon is more prevalent than its powdered counterpart with approximately 60% of the world carbon supplied in the granular form (Activated Carbon Markets, 1994). Granular carbon is more versatile than the powdered form, as it can be used in both liquid and gas phase applications (Bansal, et al., 1988). Powdered carbon is used only for adsorption in the liquid phase (Bansal, et al., 1988). Granular carbon can easily be reclaimed, reactivated and reused and depending on its degree of attrition, with little reduction in activity or mass. Powdered carbon can be reclaimed and reactivated from liquid media, but it is an expensive process that involves significant loss of carbon mass.

*Granular activated carbon for metal ion adsorption.* Metal ions are ubiquitous in nature and enter sources of water by a variety of ways, both natural and manmade. They range in toxicity from the relatively harmless calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) ions found in almost all natural sources of water, including ground water, lakes and rivers to the potentially toxic lead ( $\text{Pb}^{2+}$ ), mercury ( $\text{Hg}^{2+}$ ), cadmium ( $\text{Cd}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ) ions placed in water largely by human intervention through mining and manufacturing.

Because potentially toxic metal ions can be found in drinking water and wastewater at concentrations dangerous to human health, a low cost and effective means is needed to bring the concentrations to below levels mandated by the particular country, state or city. Activated carbon would be a possible choice as an adsorbent for this purpose, but commercial carbons are poor metal ion adsorbents (Johns, et al., 1998, Toles, et. al., 2000). Metal ions are normally reduced to safe concentrations by a combination of pH adjustment using a base such as sodium hydroxide (NaOH) or calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] to precipitate the metals in their hydroxide form and use of cation exchange resins which remove small concentrations of metal ions by means of an ion exchange process. In the ion exchange process, divalent metal ions, such as copper and zinc, replace the monovalent sodium ion on the resin's ion exchange sites. The ions are ionically bound by opposite electric charge and are not covalently bound to the resin. This combination is very effective, but very expensive, based primarily on the high cost of the cation exchange resin.

Therefore, processes that rely on the adsorption of metal ions could be made cheaper if a new, lower cost, effective adsorbent could be developed. One such adsorbent could be an activated carbon with a large negative surface charge that would enhance its adsorption or cation exchange properties of positively charged metal ions. A carbon would be a logical choice because carbons are readily acceptable adsorbents in a variety of different manufacturing processes.

Moreover, activated carbon markets, which include tertiary water treatment for municipalities, industrial wastewater treatment, domestic water filters, and food and drug purification (Activated Carbon Markets, 1994), all rely on additional water treatment chemicals to remove metal ions. If a carbon could be developed with a large negative surface charge capable of removing metal ions from solution, then, in many instances, a combination of different carbon types, one type for adsorption of organic constituents and one type for adsorption of metal ions could be used to successfully to remove a particular source of contamination, thereby relying on only on activated carbon, rather than carbon and a cation exchange resin.

From an economic standpoint, placing activated carbons in a market category that includes expensive cation exchange resins is a good strategy. The cost of the carbons would be low compared to the resins. If the carbons had metal ion adsorption properties similar to the resins, the buyer would gravitate toward the cheaper product. Additionally, placing such a carbon in the general carbon market would also be a good strategy. At present, there is only one commercial activated carbon that claims good metal ion adsorption capabilities. Therefore, the competition is minimal and the market open to the entrance of other products.

At the SRRC, the major emphasis has been on developing granular activated carbons from nutshells that can readily adsorb inorganic constituents, particularly metal ions, in addition to the adsorption of organic compounds (Johns, et al., 1999, Toles, et al., 1997, 1998, Toles, et al., 2000). All commercial carbons do an excellent job of removing organic material from either the gas or liquid phase. However, these carbons do a less than adequate job of removing metal ions from drinking water or wastewater as noted previously. Many commercial carbons that claim to adsorb metal ions are made from steam-activated coal or steam-activated peat. As mentioned earlier, the best current commercial carbon for metal ion adsorption is Minotaur. It is derived from coal, but the method of activation used in its production is a company trade secret.

Experimental carbons with particularly good metal ion adsorption that are made in the laboratory at the SRRC are derived primarily from nutshells, but we have developed activated carbons for the same purpose from wood, soybean hulls and rice hulls (unpublished results).

*Development of metal ion-adsorbing carbon.* This section of the paper describes the technology used at the SRRC for development of metal ion-adsorbing carbons from nutshells. In this section, we will also compare the physical, chemical and adsorptive properties of the carbons made in the laboratory with commercial carbons. To our knowledge, the laboratory produced carbons have the highest metal ion adsorption values compared to any commercial carbons we have evaluated and compared to any carbons described in the literature.

The metal ion-adsorbing carbons are made by a process involving phosphoric acid activation and simultaneous or concurrent air oxidation at pyrolysis/activation temperatures between 170-450°C (Toles, et al., 1998). Nutshells are soaked in 50% phosphoric acid at a ratio of one part nutshell to one part acid for a period of time between 2 and 16 hours, then charred at 170°C in an air atmosphere for one-half to one hour. The temperature is then increased to 450°C and held at this temperature for one hour in an atmosphere of compressed air. The carbon is allowed to cool in the furnace to a temperature below 100°C, then washed with hot water (80-90°C) until the phosphoric acid is removed. The phosphoric acid removed from the carbon can be concentrated to a 50% solution and reused once. Further use of the acid for activation results in a carbon product in which there is decline in the amount of metal ion that can be adsorbed by the carbon (Toles, et al., 1998). The carbon is then dried and is available for use.

*Physical, chemical and adsorptive properties.* Three important physical properties will be discussed, namely, carbon yield, surface area and attrition. A comparison between experimental carbons made from pecan shell and almond shell and several commercial carbons is presented in Table 1.

Since coal has a relatively high elemental carbon content, the yield of steam-activated, coal-based carbons (Filtrisorb 400, Hydrodarco GWC, Hydrodarco 4000) was high, and ranged from 38-48%. However, also included in Table 1 are steam activated carbons from compressed and extruded peat (Norit RO 3515) and coconut shell (Calgon GRC-20). These carbon yields were not available nor was the yield for Minotaur, which is also a coal-based carbon. The method of activation for this carbon was not known to the authors. Nutshells have a lower elemental carbon content than coal and a typical yield resulting from the acid activation process was about 35% (Johns, et al., 1999, Toles, et al., 1998, Toles, et al., 2000).

**Table 1. Physical properties (% yield, Surface area, % attrition) of phosphoric acid activated pecan and almond shell carbons and commercial carbons<sup>a</sup>.**

Carbon	% yield	Surface area (m <sup>2</sup> /g)	% attrition
<i>Nutshell</i>			
Pecan shell	35	1560	32
Almond shell	34	1280	11
<i>Commercial</i>			
Filtrisorb 400	43-47 <sup>b</sup>	948	2.5
Hydrodarco GCW	44-48	874	9.5
Hydrodarco 4000	38-43	575	36
Calgon RO 3515	Not available	794	0.0
Calgon GRC-20	Not available	928	0.0
Minotaur	Not available	750	47

<sup>a</sup>The data given in this table were taken from references 11,13 and 16.

<sup>b</sup>These values are from personal communications with the companies, Calgon Carbon Corp. (Filtrisorb 400) and Norit Americas, Inc. (Hydrodarco GCW and Hydrodarco 4000).

Surface areas for commercial carbons were in a broad range of values and the samples selected for Table 1 vary from 575-948 m<sup>2</sup>/g, while surface areas for the experimental nutshell-based carbons were very high at 1280-1560 m<sup>2</sup>/g. Phosphoric acid activation contributes to a high surface area with a high degree of microporosity when nutshells are used as a feedstock (Toles, et al., 1998).

Attrition, or the degree in which a carbon is reduced to smaller particle size through mechanical abrasion under standard test conditions, varied from 0-47% for the commercial products that we selected (Table 1). In contrast, attrition for the experimental carbons was 11-32%. These values fit into the range of attrition data exhibited by the commercial samples.

Chemical properties of carbons, which include surface charge and pH, are important in defining the ability of the carbon to bind positively charged metal ions. The extent of surface charge dictates the pH. Carbons with high negative surface charge and low pH (<4) are more likely to adsorb positively charged metal ions than a surface of low negative surface charge and higher pH (>6). The laboratory measures negative surface charge in mmoles of acid (proton) equivalents per gram of carbon on a dry weight basis or mmole H<sup>+</sup> equiv/g carbon (Toles, et al., 1999). Typical surface charge for commercial, steam-activated coal-based carbons are exemplified by Filtrisorb 400 and Norit RO 3515 with values of 0.24 and 0.00 mmole H<sup>+</sup> equiv/g carbon, respectively (Table 2). Minotaur, however, had a much larger surface charge of 2.99 mmole H<sup>+</sup> equiv/g carbon. Pecan shell- and almond shell-based carbons from the laboratory had negative surface charge values higher than Minotaur. Although pH values are not shown for the specific carbons displayed in Table 2, a typical pH range for steam-activated commercial carbons would be about 6-9. Minotaur had an acidic pH of 2.6 (Wartelle and Marshall, 2001). A pH range of 3-4 is consistent with acid-activated nutshell carbons (unpublished observations)

Adsorptive properties are dependent on the physical and chemical properties of carbons. In the case of metal ion adsorption, the overriding consideration is negative surface charge. This chemical property is critical in defining how much metal ion will be adsorbed. The laboratory studies have shown a statistically significant direct correlation between metal ion adsorption and negative surface charge (Toles, et al., 1999, Wartelle and Marshall, 2001). For commercial carbons with low negative surface charge (Filtrisorb 400 and Norit RO 3515), 0.50 and 0.24 mmoles of metal ion (copper ion) were bound per g carbon, respectively (Table 2). This can be compared to 1.13 and 1.20



**Table 2. Chemical property (surface charge) and adsorptive properties (metal ion and organics adsorption) of acid activated pecan and almond shell carbons and commercial carbons<sup>a</sup>.**

Carbon	Surface charge (mmoles H <sup>+</sup> /g)	Metal ion uptake (mmoles Cu <sup>2+</sup> /g)	Organics uptake (mmoles/g)
<i>Nutshell</i>			
Pecan shell	3.41	1.13	0.42
Almond shell	3.55	1.20	0.44
<i>Commercial</i>			
Filtrisorb 400	0.24	0.50	0.58
Norit RO 3515	0.00	0.24	Not available
Minotaur	2.99	0.95	0.59

<sup>a</sup>The data given in this table were taken from references 11, 13, 16 and unpublished observations.

mmoles of copper ion bound per g of nutshell-based product where the negative surface charge was much greater. Minotaur adsorbed 0.95 mmoles of copper ion per g, as would be expected from its high negative surface charge and low pH.

The data on organics uptake (Table 2) was included to emphasize that acid-activated carbons from nutshells have the capacity to adsorb organic compounds in addition to metal ions. In this case, a solution of six organics, which included acetone, acetonitrile, benzene, 1,4-dioxane, methanol and toluene, were evaluated as a group. The ability of the carbon to adsorb this mixed suite of compounds was recorded. Organics uptake was lower in the nutshell-based carbons than their commercial counterparts. However, all carbon were able to adsorb both types of adsorbates.

In summary, experimental carbons made at the SRRC from pecan and almond shells by the phosphoric acid activation process have lower yields, higher surface areas and similar attrition values to comparable commercial carbons made from coal, extruded peat and coconut shells. The pH tends to be lower and the negative surface charge considerably higher in the acid-activated carbons compared to most commercial products. As a result of the high negative surface charge, the carbons possess excellent metal ion adsorption properties, while most commercial carbons have poor metal ion adsorption.

We attribute the high negative surface charge to the chemisorption of oxygen on the carbon surface. In our activation process, chemisorption occurs when oxygen in the air comes in contact with the carbon surface at high temperatures. Under these conditions, a variety of surface functional groups are created, including carboxyl, carbonyl, phenolic and lactones (Toles, et al., 1999).

#### IV Carbon research at NIRE

*Carbon products from organic waste products:* The laboratory of Upland fields at the National Institute for Rural Engineering and some other laboratories in Japan have been carrying out research on the development of usage and manufacturing technologies of carbon products from agricultural byproducts and waste products since 1998. Two main uses in agriculture and the rural areas have been identified as 1) soil amendment (soil dressing) and 2) absorbent.

Carbon products are reported in the literature to have properties such as 1) low density, 2) high absorptive capacity and 3) high porosity; these properties are expected to impact the soil by improving its physical properties such as permeability and water holding capacity. Shinogi et al., 2002 found some improvements in the permeability of clay soils and concluded that the degree of improvement depends on the texture of the soil.

Also, some carbon products can absorb ammonia gas, especially carbon products from activated sludge manufactured at lower temperatures (250°C) (Yasumura, et al., 2002).

Manufacturing technology in the carbonization process requires the use of external source of energy because some of the source materials are not self-combustible. It is important to reduce the energy input involved carbonization in order to minimize the cost of production. The laboratory at NIRE has in collaboration with a private company developed a self-combustion (burnt) carbonization plant and tested it in a pilot scale. There is a possibility of adding the activation function to this plant in the future. Currently, the carbonization plant is being tested in the actual field situation.

## V Technology Transfer

Based on the findings given in this paper, we believe the nutshell-based, acid-activated carbons are excellent metal ion-adsorbing carbons and can compete with any commercial carbon that we are aware of in term of efficacy and cost. In light of these findings, the next important step needs to be considered, namely, transferring the technology to a potential manufacturer. In order for technology transfer to occur, we believe that the following four activities need to be taken into consideration: (a) exploit the availability of nutshells in countries where feedstocks, such as coal, are unavailable, (b) evaluate the activated carbon using regional sources of water or wastewater to be purged of metal ion contaminants, (c) partner with a company within the country in question, and (d) exploit the niche market for ion exchange carbons which are likely to have few competitors.

If the potential manufacturer believes your activated carbon is less costly and more efficacious than the competition, then they will be happy to initially produce sufficient carbon for evaluation by select users or customers. The demand from the consumer will be the ultimate test for your product. If demand is present, then the company can sell the product with confidence that a profit can be realized and you will have successfully transferred technology from the laboratory to the marketplace. For example, in Japan, there are many uses for activated carbon and carbon products, if less cost than currently available carbons can be achieved. It is important to remember that the technology described in this paper could be adapted to other agricultural and food industry by-products, thus making this technology very versatile.

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## 農業副産物由来の炭化物利用について

マーシャル E. ウェイン, 凌 祥之\*

### 要約

活性炭は世界でも最も利用されている吸着材である。ココヤシの実, 泥炭などの農業用副産物を原料として活性炭を製造しており, 販売にあたっては様々な観点からの評価及び検討が必要である。筆者らは主にアメリカ合衆国農務省における研究を中心に, 活性炭の金属吸着機能, それらの商業製品としての基準, 原料コストの調達難易度の観点などからそれらの商品性を評価し, 将来性を展望した。その結果, 農業副産物由来の活性炭は有望な金属イオンの吸収体であり, 効率及び製造コストの面からも商品性が高い

と考えられる。また, これら技術の民間企業への移転における問題点を抽出して整理した。更に, これら合衆国における既往の成果を, わが国の実情に合わせて技術開発し, 普及するために, 当該研究所で進めている炭化研究を概観し, 技術普及に関する問題点を検討した。その結果, 製造コスト次第では日本でも炭化物の用途は有望であると考えられる。

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