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FINAL REPORT
**GRANULATED PEAT FOR TARGETED
INDUSTRIAL APPLICATION**

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Granulated Peat for Targeted Industrial Applications

Final Report for Minnesota Technology, Inc.

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Objective: To develop and commercialize an effective absorbent peat granule for use in removing metals and hydrocarbons from wastewater and as an industrial oil absorbent.

Background: Extensive research has focused on raw peat for removing contaminants such as dissolved metals and organics from wastewaters. Peat has significant cation exchange capacity due primarily to the carboxyl groups of its humic acid constituents. Efforts to capitalize on peat's natural exchange capacity for industrial use has been hampered by the impermeability of peat to water flow, the tendency of organic matter to leach from peat, the instability of peat at pH values above eight and its high dust content in dried form. Studies conducted by the Natural Resources Research Institute (NRRI) in conjunction with Peat Technologies Corporation have focused on solving the impermeability, leaching, stability and dust problems associated with using peat on an industrial scale. The focus of these efforts have been to specify a granulation process and to identify test markets where granulated peat can be used. The granulated peat is specifically targeted for use as a general purpose oil absorbent and as a filtration media for removing contaminants from wastewaters.

A laboratory-scale process for granulating peat into a permeable, non-leaching and stable granule was developed at NRRI. The process appears to offer high throughput potential and produces structurally stable particles with desirable sorption characteristics. The major thrust of future research is to scale-up the technology to pilot-scale to demonstrate the process and provide enough material for field trials throughout industry. Once successful field trials are realized, Peat Technologies Corporation plans to bring in second tier investors to their core investor group.

Progress/Results:

GRANULE FABRICATION PARAMETERS

The key operating variables for granulating peat into a highly porous and stable granule were identified. These variables included feed pressure, shear speed, feed consistency, peat type, and curing method. Uniformity and granule density are controlled by these variables. The specifics of the process cannot be discussed because the feasibility of obtaining a University patent is currently being reviewed.

OIL SPILL MAINTENANCE MARKET

The two most important performance criteria associated with the use of loose peat in existing markets are sorbency and product dustiness. Granulating loose peat may improve on both of these performance criteria. The test methods chosen for evaluating these criteria were sorbency and dust index. Federal Sorbency Specification (Method PA-1056B) was used to measure the volume of oil sorbed by the granulated peat. Dust levels were measured by a modified ASTM procedure D547-41, a commonly used method for measuring coal dust in the coal industry.

The most desirable characteristic of a granulated peat would be to improve dustiness and sorbency simultaneously. Results have shown that although granulation reduces dust significantly, a slight decrease in sorbency is also realized because of the greater density of the produced granules. Generally, a 35 percent decrease in sorbency was realized while improving product dustiness nearly 325 percent over loose peat. Many attempts were made to balance this trade-off by varying the method in which the granules were produced. However, a more favorable trade-off could not be identified. Therefore, the 35/325 percent trade-off was considered acceptable for test marketing.

The granulated peat with the least amount of dust and greatest sorbency were Sphagnum type peats. Sphagnum peat from Peatrex Peat Company near Cromwell, Minnesota, was shown to have the best sorbency with minimal dust. The sorbency of this peat after granulation was 2.60 ml/gm, versus 4.0 ml/gm for ungranulated loose peat. The dust indices for granulated versus ungranulated peat were 0.012 gm dust/1000cm³ and 0.051 gm dust/1000cm³, respectively.

Several samples of granulated peat were sent to Fisher-Stevens Inc. and American Cellulose for application in the oil sorbent market. Their review of the product was not favorable, mostly due to decreased sorbency compared to loose peat. In addition, they felt the improved dustiness of the granulated peat could not overcome its reduced sorbency and higher cost. They indicated increased levels of competition in their market segments as factors for the marginal review of the product. Bio-based materials such as corn, recycled paper residues, and new lighter weight clays have gained significant access into their markets resulting in fierce pricing competition. In light of this review more emphasis was put into the development of the wastewater treatment market.

WASTEWATER TREATMENT MARKET

For peat to be used as a sorption media for removal of heavy metals from wastewaters, it must be able to withstand repeated sorption/desorption cycles, resist mechanical breakdown, and resist swelling and plugging when subjected to contaminated water flows. In addition, it must be a significantly cheaper alternative than conventional technology.

As a preliminary evaluation of these characteristics, a reed sedge and Sphagnum peat were granulated and tested for metal sorption and flow characteristics. Several preliminary sorption tests were conducted. Dilute solutions of Zn⁺⁺, Pb⁺⁺, Fe⁺⁺ and Cr⁺⁶ were passed through columns containing granulated peat specifically sized at -2.00 mm to + 0.85 mm. The purpose of this test was to demonstrate the feasibility of using granulated peat for removing metals from dilute solutions. Also, this test provided information on the physical stability of the granules and swelling or compaction in a filtration column.

The results of these trials demonstrated the capacity of granulated peat to adsorb dissolved metals in water. Removal efficiencies of greater than 97 percent were achieved for these metals when challenged with 10 ppm feed water solutions containing all of the above metals. Discharge criteria for chromium and zinc were easily achieved (<0.23 ppm Cr^{+6} , <1.5 ppm Zn^{++}). These tests also revealed that moderate leaching of color occurred and that the strength properties of reed sedge peat were superior to that of Sphagnum peat. These factors were considered as the more detailed test program was developed.

Because Minnesota peats can vary according to botanical origin and degree of decomposition, an analysis was done to quantify variation in cation exchange capacity of selected peats. Results have shown that the peat resource available to Peat Technologies Corporation has cation exchange capacities in the range of 130 to 150 milliequivalents/100 gms (measured as barium meqs. at pH 8). This reed sedge type peat had one of the highest CEC's of the five peats tested. These results helped show that peat selection is critical and governs the performance that can be expected from any given peat source.

Stability was evaluated by high velocity water washing and dry crush strength. The breakdown of particles greater than 60 mesh, when subjected to a high velocity (5 ft/sec) water wash for four hours consistently averaged less than 6 percent. This is a worst case scenario as these velocities are much higher than what would be encountered in commercial application of treatment media. To supplement these tests, the dry crush strength of randomly selected particles were also measured by an Instron Tensiometer. Dry crush strength consistently averaged four to six pounds force which is about the same force required to break a clay based granule. Physical stability, resistance to breakdown, and crush strength are important characteristics for filtration media as industrial process water streams have high velocity fluctuations and high flow rates. The granules seemed to meet these requirements. An interesting note to these findings was that granule stability could be improved significantly by altering the curing method.

Further evidence of granule stability was demonstrated in column mode for various metal-laden feed waters at pH ranges from four to eight. Throughout these tests, visual evidence of physical breakdown of the granules was minimal.

Use of granulated peat in commercial applications requires that the rate of adsorption of contaminant onto the peat be relatively fast. Adsorption isotherms indicated that essentially 90 percent of equilibrium adsorption is achieved in the first 20 minutes of contact. This minimizes column height and shows that the process of granulation minimizes densification and the porous nature of peat is maintained.

To further identify the effects of curing method on the sorption and stability of granulated peat, multiple sorption columns containing granulated peat were challenged with feedwaters containing 10 ppm of Ba^{++} , Fe^{++} , Ni^{++} , Zn^{++} , Pb^{++} , Cu^{++} , and Cr^{+6} . Two sets of sorption columns, each containing granulated peat cured by different methods were challenged with identical feedwaters. Columns were run in triplicate. The results showed that a higher degree of sorption was obtained with the first curing method versus the second method.

Recovery of sorbed metals through acid-washing can be an important factor in certain treatment applications. Stripping the sorbent of heavy metals allows re-use of the media for multiple cycles thereby decreasing treatment costs. Recovery of sorbed metals was demonstrated by stripping a saturated column with 0.1N H₂SO₄. Sulfuric acid was chosen as the eluant because it was cited as the most effective in other tests and is compatible with most process streams. Results showed that nearly 100 percent of the sorbed metals were recovered. This observation is supported throughout the literature (Jeffers 1991, 1993; Grishakov 1990).

Removal of de-icing agents such as ethylene glycol (EG) from airport run-off is likely to receive increased scrutiny (personal communication, STS Consultants). Results have shown that at a heavy loading of 83,000 mg/l EG, peat is able to absorb 0.65 gm EG/gm peat indicating it may have potential for removal of this contaminant.

An economic comparison to conventional technology is difficult because most wastewater cleanup applications are site specific. However, if peat granules are to be successful in the marketplace, relevant cost and performance data must be developed. A commercially available cation exchange resin was selected for a comparative analysis of cost and performance relative to peat granules. Retail costs for the resin were quoted by manufacturers representatives and averaged \$165/ft³. Using the resin as the performance standard, granulated peat has about 59 percent of the resin's exchange capacity on a dry weight basis (125 avg meq./gm vs. 209 meq./gm). Because of this, costs of granulated peat must be significantly less than synthetic resins. Our analyses show that granulated peat would have to retail for approximately \$26 per ft³ to be 20 percent more cost effective than the resin. Costs of horticultural peat currently range from \$4 and \$5 for a 4 ft³ bale. This is equivalent to \$1 to \$1.25 per ft³. This analysis does not account for the wide array of contaminants that granulated peat is able to sorb and its specific selectivity for toxic metals over less harmful cations such as Ca⁺⁺, Mg⁺⁺, and Na⁺ ions. The binding of Ca⁺⁺ or Mg⁺⁺ to ion exchange resins often limits the usefulness of resins in mixed wastewaters since they compete with more toxic metal ions for exchange sites.

Conclusions: A process for granulating peat was identified at the laboratory-scale level. The process produces a highly porous, structurally stable peat granule with no significant reduction in cation exchange capacity compared to unprocessed peat. This process was successfully scaled-up to produce sufficient quantities for market testing. Tests showed that peat type and curing method affects performance. The granules were found to be effective in removing a wide array of metals and ethylene glycol from water and can potentially be used as a general purpose oil absorbent. The viability of the technology appears promising. Peat granules may have significant potential value in the low cost treatment of polluted waters and in the general cleanup of spilled oil. Future research is focusing on considerations for scale-up of the technology, identification of market niches where this type of technology could compete effectively and in development of field trials. Peat Technologies Corporation is actively pursuing a private licensing agreement in cooperation with NRRI to promote and develop this technology further.