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Formulation of a biodegradable, odor-reducing cat litter from solvent-extracted corn dried distillers grains☆

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ABSTRACT

Cats are among the most popular pets in the U.S., and the majority of these animals are kept indoors where litter boxes containing some type of absorbent litter material are needed. Dried distillers grains (DDGs) are a major co-product of the ethanol industry, and are primarily sold as animal feed. We have been studying value-added uses for DDGs by extracting valuable phytochemicals from them with a variety of organic solvents. The objective of this research was to determine if the extracted DDGs could be formulated as cat litter. Extracted DDGs absorbed significantly more water (termed hydration capacity) than unextracted DDGs, although sorting the extracted DDGs by particle size had no effect on hydration capacity. Through the addition of glycerol as a dust retardant and guar gum as a clumping agent, a formulation was obtained with desirable physical properties. The addition of copper sulfate to this formulation significantly reduced the release of a volatile odor compound that is chemically similar to the odor compound produced by the decomposition of cat urine. From these results it appears that extracted DDGs have potential as commercial cat litter.

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1. Introduction

Domestic cats are among the most popular pets in the U.S., with over 93 million animals being owned according to a recent survey by the American Pet Products Association (APPA, 2010). Because the majority of these cats live primarily indoors, litter boxes containing some type of absorbent litter material are needed (Neilson, 2009). Each day the average cat generates approximately 40 g of fecal waste, meaning that the annual fecal production for cats in the U.S. is over 1.18 million metric tons (Dabritz et al., 2006). The most recent study conducted found that approximately 60% of the cat litter sold in the U.S. consisted of clumping clay, most of which is composed of bentonite clay (Yarnell, 2004). Sodium bentonite clay is able to absorb more water than bentonite clay containing other ions, such as calcium, so that sodium-rich bentonite is therefore the material of choice for clumping cat litter (Virta, 2005). A negative aspect of these clumping clay litters is that they do not decompose and are not recommended to be flushed into either sewage or septic systems by the manufacturers. Additionally, there have been reports of illnesses and deaths in cats from inhalation and/or ingestion of clumping clay litters (Michaels, 1995; Hornfeldt and Westfall, 1996).

Plant product-based alternatives to clumping clay kitty litters have been commercially available since the 1980s. These litters consist of a variety of materials, including sawdust, wheat, alfalfa, oat hulls, corn cobs, peanut hulls, or recycled newspaper (Yarnell, 2004; Neilson, 2009). Unlike clay-based litters they can be flushed into sewage and septic systems, although disposal of cat fecal material in this manner has been implicated in the infection of southern sea otters (*Enhydra lutris nereis*) by the parasite *Toxoplasma gondii* along the California coast (Miller et al., 2002). Infection of humans with *T. gondii* via exposure to cat fecal material has also been reported (Dabritz and Conrad, 2010). On the plus side, unlike clay-based litters, some of these litters are advertised as safe for the cats to eat (Yarnell, 2004).

Dried distillers grains (DDGs), also called distillers dried grains with solubles, are one of two major co-products remaining from the dry-grinding process for ethanol fermentation from corn, the other being carbon dioxide (Rosentrater, 2006). Most of the DDGs produced in the U.S. are used as animal feed, and as such have relatively low economic value. Finding higher value uses for co-products is vital for the success of the ethanol industry, and recent efforts have focused on using biofuel coproducts such as DDGs as raw materials for new industrial products (Mohanty et al., 2009).

The authors have been studying extracts from DDGs as potential sources of phytosterols, steryl ferulates, tocopherols, tocotrienols

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and carotenoids for food and nutraceutical uses (Winkler et al., 2007; Winkler-Moser and Vaughn, 2009). These compounds are valued as antioxidants for food oils and for their overall health-promoting/disease-preventing activities. In the above studies, after the extraction process was finished, an additional coproduct was obtained, extracted DDGs (x-DDGs). We found that these x-DDGs had excellent water absorption, and due to their physical similarity to several commercial cat litters, we decided to study the utilization of x-DDGs as potential cat litter.

2. Materials and methods

2.1. Solvent extraction and size separation of DDGs

DDGs from whole kernel corn were obtained from Big River Resources LLC, West Burlington, IA. DDGs were extracted for 24 h with hexane (Fisher Scientific, Fair Lawn, NJ) using a Soxhlet apparatus to remove oil and other lipophilic constituents to produce 10.0 kg of x-DDGs. The unextracted DDGs contain on average 10.5% hexane-extractable compounds, most of which are triglycerides with a small percentage of free fatty acids and other lipophilic compounds such as tocopherols, tocotrienols and steryl ferulates (Winkler-Moser and Vaughn, 2009). The unextracted DDGs have a distinctive odor of fermentation when dry and which becomes increasingly more intense upon wetting, and the extraction process eliminates this problem (unpublished data). x-DDGs were placed in a drying oven for 24 h at 45 °C to remove any residual hexane. After drying, 5.0 kg of the x-DDGs were size separated using a Rotex® gyratory screener (Rotex Global LLC, Cincinnati, OH) equipped with an 18-mesh screen to determine if particle size influenced hydration capacity. These x-DDG fractions were separated into large (remained on the top of the screen; 2.9 kg) x-DDGs and small (passed through the screen; 2.1 kg) x-DDGs.

2.2. Hydration capacities and bulk densities of unextracted and solvent extracted DDGs

Hydration capacity, which is defined as the ability of a solid matrix to absorb liquids, was calculated by using a modified version of the American Association of Cereal Chemists Method 56-20, Hydration Capacity of Pregelatinized Cereal Products (AACC, 2003). Hydration capacity data for unextracted DDGs, x-DDGs, large x-DDGs and small x-DDGs were obtained via this method using 1.0 g samples placed in 15 ml centrifuge tubes. Ten ml of ddH_2O was added to each tube and the samples were shaken on an orbital shaker set at 250 rpm for 15 min. The tubes were then centrifuged for 15 min at 1000 × *g*, the supernatant carefully decanted, and the tubes weighed. The hydration capacity was the weight of the tube and wet sample minus the weight of the tube divided by the dry sample weight.

Bulk densities were determined by introducing 100.0 g of the test sample, *M*, into a dry 100 ml graduated cylinder. The unsettled apparent volume, V_o, was measured to the nearest graduated unit. The bulk densities of the samples, in g ml^{-1}, were determined by the formula: $(M)/(V_o)$. All samples were run in quadruplicate for both hydration capacity and bulk density.

2.3. Clumping of litter formulations

To the best of our knowledge there are no published/standardized tests for cat litter clumping ability, so we developed a simple test to quantitate clumping of our litter formulations. Initially, glycerol (500.0 g; Craft Lobby, Memphis, TN) was heated to ~95 °C in a water bath, which significantly reduced the viscosity of the glycerol, allowing it to be easily mixed with the x-DDGs. Guar gum (50.0 g; Natural Foods, Inc., Toledo, OH), which is a commonly used clumping agent for commercial cat litters, was added to the glycerol and continuously stirred to form a homogeneous suspension. The glycerol acted as both an agent to adhere the guar to the x-DDGs as well as preventing dust formation. x-DDGs (100.0 g samples) were then thoroughly mixed with 10.0, 25.0, 50.0 and 100.0 g, respectively, of this solution, and placed in a drying oven set at 30 °C for 24 h before further testing. Clumping activity was determined by adding 5.0 g of each treatment into plastic petri plates (60 mm × 15 mm BD Falcon™, Becton Dickinson, Franklin Lakes, NJ, USA), then allowing 5.0 ml of water to drip into each plate from a 100 ml burette (Cole-Parmer, Vernon Hills, IL). Plates were then placed in a drying oven set at 30 °C for 24 h. The contents of each plate were then emptied onto a 6 mesh sieve (which was sufficiently large to allow passage of all unclumped x-DDGs) and placed on an orbital shaker set at 250 rpm for 1 min. Clumping percentage was calculated as follows:

$$\text{clumping percentage} = \left(\frac{\text{weight of clumps retained on 6 mesh sieve}}{5.0\,\text{g}}\right) \times 100\%$$

All tests were run in quadruplicate.

2.4. Effect of $CuSO_4$ on odor volatile absorption by litter formulations

Cat urine contains several species-specific odor compounds which are used as territorial markers, including the thiol compound 3-mercapto-3-methyl-1-butanol (Miyazaki et al., 2006). Divalent copper compounds such as copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$; CSP) have been found to form very stable complexes with thiols (Leal and van den Berg, 1998). An experiment was conducted to determine the effect of CSP on headspace concentrations using solid phase microextraction (SPME) analyses of a volatile thiol compound. Because 3-mercapto-3-methyl-1-butanol is not commercially available, we used a chemically similar thiol compound, 3-mercapto-2-butanol (Sigma–Aldrich). A solution was prepared by mixing 100 mg of CSP with 100 ml of hot (95 °C) glycerol until it had dissolved. After mixing, 10 g of guar gum was added to the solutions and constantly stirred before applying to x-DDGs at the rate of 25 ml solution/100 g x-DDGs. This produced x-DDGs with a copper sulfate concentration of 125 ppm. A control litter formulation was prepared by adding the same rate (25 ml solution/100 g x-DDGs) of a glycerol/guar gum solution lacking added CSP. Both formulations were placed in a drying oven set at 30 °C for 24 h before further testing. Headspace analysis vials were filled with 1.0 g samples of both treatments, and 0.2 ml of a solution of 1 mg/ml 3-mercapto-2-butanol in ddH_2O was added. The vials were capped, shaken vigorously, and incubated at 25 °C for 24 h. Headspace concentrations of 3-mercapto-2-butanol were analyzed by automated SPME using a Varian Combi-Pal SPME autosampler connected to a Varian 3800 GC with helium as the carrier gas (1 ml/min), and an FID detector (280 °C). Sample vial septa were pierced with a SPME needle with a retractable 50/30 μm divinylbenzene/Carboxen™ on polydimethylsiloxane coated fiber (Supelco, Bellefonte, PA). The fiber was exposed to the headspace for 10 min at 25 °C, then retracted and immediately injected and desorbed for 5 min in the GC injector port. Volatiles were separated on a DB-5 (30 m × 0.25 mm i.d. 0.25 μm) column (Agilent, Santa Clara, CA) using a temperature program of 40 °C for 1.5 min, 20 °C/min to 250 °C where it was held for 5 min. Injection was splitless until complete desorption (5 min) followed by split (1:50). Two 3-mercapto-2-butanol isomer peaks were identified by comparison of retention time to commercial standards diluted in ddH_2O. Headspace analysis of x-DDGS with no added 3-mercapto-2-butanol was also performed to verify that there were no interfering peaks at the same retention time. Peaks