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Review article

Surface-active physicochemical characteristics of spent bleaching earth on soil-plant interaction and water-nutrient uptake: A review

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ABSTRACT

The activated or neutral form of bentonite-based spent bleaching earth/clay (SBE) is a by-product generated during the bleaching process in edible oil refinery. Its untreated form is disposed of directly at landfills involving high cost and land area, and possibly causing environmental problems. Recently, this undesirable dumping exercise has been prohibited. To overcome this, SBE is regenerated and reused for value addition, e.g. as bio active materials for water/wastewater treatment. A more recent approach being converting SBE into bio fertilizers; of which the fertilizer characteristics in relation to physical, chemical and biological interaction with soil and its surrounding ecosystem (nutrients, water, pollutants, microorganisms, climate, etc.) is vital in agricultural applications associated with soil fertility management and crops productivity. Previously, SBE's structural characteristics, surface chemistry and activation have been disclosed. This paper provides an insight on soil-crop interactions and agronomy with SBE functions as a soil amendment.

Contents

1. Introduction

For centuries, man has been applying agro-industrial wastes on land as fertilizer or just to dispose of them, e.g., plant residues, animal manures, fly ash from thermal power plants, grape wastes from wineries,

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etc. (Khalid et al., 2000; Arvanitoyannis et al., 2006; Jala and Goyal, 2006 and Petric et al., 2009).

Among the world's major 17 edible oils and fats, palm oil is the largest, constituting 62.8 million t or one-third of the world production (MPOB, 2016), mainly from three major producers - Indonesia, Malaysia and Thailand. As the world's second largest grower, Malaysia produced ~20 million t from ~56,000 km^2 (5.64 million ha) of oil palm plantations, or about 32% of the world supply (MPOB, 2016). In palm oil extraction, vast amount of by-products are generated (Boey et al., 2011; Loh et al., 2013; Kong et al., 2014 and Liew et al., 2015). In particular, the crude palm oil (CPO) produced is refined before use, which, process is, inter alia, bleaching with a surface-active substance, usually a clay-based bleaching earth - to adsorb the impurities although other adsorbents such as activated carbon and silica hydrogel can also be used (Gunstone et al., 2007 and Hussin et al., 2011).

In this review, *bleaching earth* refers to bentonite clays of mainly montmorillonite (Mt) - natural/raw (e.g. fuller's earth) or activated - having the capacity to adsorb coloring matter i.e. pigments and the undesirable residues from the edible oil processing, such as soap, trace metals, phospholipids, oxidation products and polyaromatics (Loh et al., 2006; Soda et al., 2006 and Hussin et al., 2011). The fully adsorbed earth is termed *spent bleaching earth* (SBE). Other industries that use similar functionalized materials for refining/bleaching include wineries, but their spent material is known as *acid waste bentonite* (AWB). Both of them belong to the 2:1 dioctahedral phyllosilicates group due to their similar arrangement of silicate and alumina components in a specific orientation, hence do not differ much in their adsorption capacity.

Globally, based on a 1 mass% bleaching earth usage for some 200 million t of edible oils and fats refined, an estimated 2 million t of SBE equivalent is available yearly (Loh et al., 2013; Beshara and Cheeseman, 2014 and MPOB, 2016). In Malaysia, ~10–15 kg bleaching earth per t CPO (1–1.5 mass%) is used in palm oil refining. This alone generates up to 240,000 t/yr SBE (Boey et al., 2011; Loh et al., 2011 and Loh et al., 2015). In the past, research mainly looked into improving the surface activity and adsorption capacity of the clay minerals via structural modification and surface reactivation (Pollard et al., 1993 and Hussin et al., 2011), and recovering the residual oil in the SBE (Al-Zahrani and Daous, 2000; Lee et al., 2000 and Loh et al., 2006) via solvent extraction and other environmentally-friendly means. SBE normally contains ~20–40 mass% in residual oil and in some cases, up to 72 mass%. It is usually disposed of directly in a landfill, either dry or as a slurry (Loh et al., 2006; Ho et al., 2010 and Meziti and Boukerroui, 2011). Attempts to extract the oil have also not proven particularly successful as the oil is of low quality containing free fatty acids, oxidation products, trace metals, etc. and cannot be used as food, and so cannot command a good price.

The excessive use of clays in oil refining poses issue in its disposal and the cost involved. The high oil content of SBE is an environmental hazard as the oil can rapidly oxidize to the point of spontaneous ignition via clay-catalyzed auto-oxidation reactions, posing fire hazard particularly if the oil is highly unsaturated (Pollard et al., 1993 and Boey et al., 2011). Besides, such disposal also poses a potential hazard to aquatic life as the containing fatty materials can leach into water (Lee et al., 2000). In view of the increasing disposal costs of SBE coupled with stringent regulatory requirement, efforts have been made to transform it into a useful product(s).

The potential uses of SBE are as (1) animal feed (Ng et al., 2006 and Damodaran, 2008), (2) adsorbents via thermal, physical and chemical reactivation (Pollard et al., 1993; Ma and Lin, 2004; Gunstone et al., 2007; Wambu et al., 2009 and Mana, et al., 2011) and pyrolysis (Tsai et al., 2002), (3) raw materials for making cement and bricks (Beshara and Cheeseman, 2014 and Eliche-Quesada and Corpas-Iglesias, 2014), (4) expanded clay granules for the construction industry and gardening (Gunstone et al., 2007), (5) fermentation facilitator in biogas plants (Gunstone et al., 2007), (6) fuel briquettes (Suhartini et al., 2011) and (7) soil improver in agriculture, etc. Of these, the last is the most researched today, even for AWB, owing to their naturally inherited nutrient-binding properties as proven in several field trials conducted on intended crop species (Croker et al., 2004; Soda et al., 2006; Arias-Estévez et al., 2007; Ho et al., 2010; Wang et al., 2010 and Loh et al., 2013). Although activation of SBE as adsorbents is the most widely practiced, the presence of contaminants such as soaps or phosphatides in residual oil of SBE would cause vitrification, thus loss of surface and bleaching activity of the thermally-treated adsorbents (Gunstone et al., 2007). The liquid residual oil, on the other hand, can be used as a substrate for (1) edible fungi fermentation to produce riboflavin as medicine, food and fodder use (Park and Ming, 2004), (2) biofuel (Lara and Park, 2004; Loh et al., 2006; Dwiarti et al., 2010 and Boey et al., 2011), (3) biolubricants (Loh et al., 2007), (4) industrial grade oleochemicals (Chanrai and Burde, 2004) and (5) animal feed (Damodaran, 2008). In the case of AWB, it has been readily used in its disposed form for direct application to soil without further treatment (Arias-Estévez et al., 2007 and Pateiro-Moure et al., 2009).

In gist, the difficulty in recovering/reusing SBE makes dumping the solid (de-oiled) residue the only practical way of disposal. Interest has thus been generated in using it, either uncomposted or composted, as a fertilizer/soil amendment to nurture plant, improve soil quality and promote microbial rejuvenation (Gunstone et al., 2007). However, even the simple application of SBE to the soil, more so if well-composted, has its risk of potential adverse effects on the soil, environment and food safety due to its possibly high heavy metals content. One the other hand, a poorly composted SBE might affect crop productivity and farmers' well-being. Therefore, a proper assessment of its suitability as fertilizer/soil amendment is of utmost importance if it is to be used this way. This paper reviews the key physicochemical characteristics of SBE for agricultural use, and its potential agronomic benefits.

2. Characteristics of SBE and its effects on soil properties

2.1. Physicochemical properties

According to Gunstone et al. (2007), bentonite from open pits is mainly Mt., a complex alumino-silicate based clay mineral from the smectite (Sm) group produced by in situ devitrification of volcanic ash. Other minerals such as beidellite (Bd), saponite (Sp), hectorite (Ht), illite (I), kaolinite (Kaol), gypsum (Gp) and quartz (Qz) are also present in smaller quantities. Two types of bleaching earth – usually bentonite-based clay containing mainly SiO_2 (65–75%) and Al_2O_3 (15–20%) - are sold commercially i.e. the virgin and acid-activated clay (Ho et al., 2010). The latter has higher adsorption than the virgin type as it is activated - the octahedral metal cations (Al^{3+}, Fe^{2+} and Mg^{2+}) exchangeable sites in the interlayer bentonite back-bone are dissolved and replaced by protons (H_3O^+) in the acid treatment (Hussin et al., 2011). This commonly used bleaching earth in crude edible oil refineries is essentially SBE.

Physically, the colour of activated bleaching earth is white, turning brownish after bleaching. The particles are very fine, mostly irregular in shape and porous. The original Mt has a total pore volume of 26.5 μL g^{-1} (Weng and Pan, 2007) with a low specific surface area of 40–160 m^2 g^{-1} (Hussin et al., 2011) while the activated one is much higher 150–350 m^2 g^{-1} (Gunstone et al., 2007; Weng and Pan, 2007 and Hussin et al., 2011). Generally, the increase is due to the acid attack and heat at the exchangeable sites which dissolves the impurities

Table 1
Chemical compositions (mass%) of spent bleaching earth (SBE).

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Reference (author, year)
79.8	8.7	1.9	3.2	0.7	Lara and Park (2004)
56.9	9.24	8.27	4.32	3.9	Loh et al. (2013)
37.45	8.01	0.83	1.28	0.78	Mana et al. (2011)
65–75	15–20	2	2.5	0.5	Weng and Pan (2007)