Industrial Crops and Products 98 (2017) 25–28

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Short communication

Assessment of lignocellulosic nut wastes as an absorbent for gaseous formaldehyde

B.K. Stefanowski[a,*], S.F. Curling[a], G.A. Ormondroyd[a,b]

[a] The BioComposites Centre, Bangor University, Bangor, Gwynedd, LL57 2UW, United Kingdom
[b] Department of Architecture and Civil Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, United Kingdom

ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form 10 January 2017
Accepted 11 January 2017

Keywords:
Nut waste
Dynamic vapour sorption
Formaldehyde
Kjeldahl
Absorption

ABSTRACT

Indoor air quality is of growing concern with a current focus on formaldehyde emissions and sick building syndrome (SBS). One of the main approaches to reduce indoor pollutant concentrations has been to reduce formaldehyde use and emissions from products. Another approach is the potential of materials to act as scavengers to actively sequester formaldehyde from the indoor atmosphere. This paper evaluates the use of the shells of various types of nuts, which are an abundant agricultural waste material. Nut shells were exposed to gaseous formaldehyde using a Dynamic Vapour Sorption system and their nitrogen content determined using the Kjeldahl method. It was found that formaldehyde absorption increased with increasing nitrogen content and that walnut shell, peanut shell and sunflower seed shell could absorb significantly higher quantities of formaldehyde gas than a sheep wool control.

1. Introduction

Indoor air quality and the effects of airborne contamination on human health, has been of growing concern in recent years (Mitchell et al., 2007; Salthammer et al., 2003; Takeda et al., 2009). It was reported that a significant proportion of the population suffer from eye and respiratory discomfort, headaches and feeling of lethargy linked to poor indoor air quality (Haghighat and De Bellis, 1998). This situation is now referred to as sick building syndrome (SBS) (Zhang and Xu, 2003). Formaldehyde (CH_2O) has been the focus of many investigations as it contributes to poor indoor air quality. Formaldehyde occurs naturally in the environment and is present and reversibly bound in all biological material (Trézl et al., 1997) and is used in many industrial products emit formaldehyde from textiles to disinfectants. A major source of formaldehyde is in pressed wood products, used in construction and furnishings (Hun et al., 2010; Kim et al., 2010). Current guidelines stipulate a limit of 0.1 mg/m^3 in interior air to avoid adverse health effects (WHO, 2010). Historically there has been considerable research into the reductions of formaldehyde emissions from their original source, namely replacing formaldehyde based resins with bio-based resins (Jiang et al., 2002; Pratelli et al., 2013). Another method is to actively modify a product to sequester VOCs, for example using cost effective lignocellulosic scavengers (Kim, 2009).

Edible nuts are grown and cultivated in a variety of climates around the world on different scales. This enormous production of nuts every year generates a considerable amount of lignocellulosic waste. Table 1 summarises the cultivation, annual seed and waste production and uses of 6 globally popular edible nuts. All of the mentioned wastes have demonstrated the potential to be used as an activated carbon for absorbing pollutants: walnut can be used as absorbent of copper ions (Kim et al., 2001), pistachio nut can remove organic compounds from air and water (Nor et al., 2013; Tavakoli Foroushani et al., 2016), coconut can remove methylene blue in aqueous solutions (Tan et al., 2008), sunflower seed shell (el-Halwany, 2013) and peanut shell can act as absorbents of CO_2 (Deng et al., 2015). This paper aims to evaluate and describe the potential of using these 6 promising agricultural wastes, in their natural, solid state for the adsorption of formaldehyde from the atmosphere to improve indoor air quality.

It is known that formaldehyde is highly reactive to proteins (Mansour et al., 2016) and reacts with the side chains of amino acids and amido groups of glucose (Curling et al., 2012). The nitrogen (protein) content was therefore determined to assess correlations with formaldehyde sorption. It is known that wool fibre will absorb formaldehyde (Curling et al., 2012) by physisorption, (absorbed into micropores within its structure) and chemisorption (forms a stable bond with the fibres). Wool fibre has therefore been used in this study as a comparative control.

* Corresponding author.
E-mail address: b.stefanowski@bangor.ac.uk (B.K. Stefanowski).

http://dx.doi.org/10.1016/j.indcrop.2017.01.012

Table 1
6 Major edible nuts, their source and annual production.

Nut	Sourced	Annual production	Waste
Almonds (*Prunus dulcis*)	Grown worldwide. North America, California greatest producer[4] (>637,000 t/year)[2]	2.09 million tonnes[1]	0.7–1.5 million tonnes waste per year and has little industrial value[1]
Walnut (*Juglans regia*)	17 major producers[3]. China largest producer (410,000 t/year)[5], North America the 2nd (300,000 t/year)[16] and Iran is the 3rd (150,000 t/year)[3]	1.48 million tonnes[3]	Multitudinous uses from dye in cosmetics, used in insecticides, fillers, asphalt, glues[4] and improving tyre grip[3]
Pistachio (*Pistacia vera*)	Grown mainly in Iran, Turkey and North America. Iran alone producing (>250,000 t/year)[7,8]	489,000 t[6]	Little industrial value, sent to landfill or burnt[19] and small use in mordant[4] and colouring and glues[20]
Coconut (*Cocos nucifera*)	Indonesia is the leading producer, followed by Philippines, India and Sri Lanka[16]. Malaysia alone requires 151,00 ha of land for production[9]	5.5 million tones[16]	Husk used for rope and matts and core can be used as peat substitute[18]. 13.6–18.14 million tonnes husk waste per annum[17]
Peanut (*Arachis hypogaea*)	Grown worldwide. China 1st in production accounting for 40% of global production[10] (14.5 t/year), followed by India (23%) [12].	32.22 million tonnes (including shell)[11]	Largely sold in shell or sent to landfill
Sunflower seeds (*Helianthus annus*)	Grown worldwide. North American alone produces 1.72 million tonnes/year[15]	27 million tonnes[13](Almost exclusively cultivated for oil[14])	Small value, sent to landfill or used as low grade roughage for livestock[15],

Data derived from: (Pirayesh and Khazaeian, 2012)[1], (Jayasena, 2016)[2], (Malhotra, 2008)[3], (Wickens, 1995)[4], (Sze-Tao and Sathe, 2000)[5], (Kahyaoglu, 2008)[6], (Kashaninejad et al., 2006)[7], (Razavi et al., 2007)[8], (Tan et al., 2008)[9], (Diop et al., 2004)[10]. (Zhang et al., 2012)[11], (Zhang et al., 2013)[12], (Li et al., 2011)[13], (Hameed, 2008)[14], (Kamireddy et al., 2014)[15], (Anirudhan and Sreekumari, 2011)[16], (van Dam et al., 2004)[17], (Konduru et al., 1999)[18], (Tavakoli Foroushani et al., 2016)[19], (Fadavi et al., 2013)[20].

2. Materials and methods

2.1. Nut shell waste and wool

The shell material was dry and oil free and crushed into small pieces (<3 mm) and removing any contaminating (non shell) material. Scoured wool fibre was also analysed as a control material for formaldehyde absorption. Urea is a very common chemical added to materials used to absorb free formaldehyde emitted from formaldehyde based products such as particleboard. However the purpose of this study is to evaluate the potential of lignocellulosic wastes used as a protein additive, to absorb ambient formaldehyde emitted from external sources other than reducing a products' formaldehyde emissions. As such, urea is beyond the scope of this study.

2.2. Dynamic vapour sorption (DVS)

Prior to the experiment, the nut shells and wool were conditioned at 23 ± 1 °C and 60 ± 3% RH until constant mass was obtained. Sorption analyses were performed using DVS system (Surface Measurement Systems, London, UK) in accordance with the methodology described by Curling et al. (2012). Three replicates were conducted for each sample.

2.3. Nitrogen content

To determine the nitrogen content of the waste nut shells, the Kjeldahl method was used. Three replicates were completed for each nut shell and wool.

The shell materials were prepared by dry milling the shells into <5 mm pieces and removing any contaminating material. The material was then oven dried overnight in a 50 °C oven. Between 0.2 g and 0.3 g of the oven dried waste shell, weighed to four decimal places, and were placed into digestion tubes to which two Kjeldahl peroxide tablets and 12 ml of sulphuric acid were added. The digestion tubes were then placed in a preheated (420 °C) digester and left to digest for 1 h from time of first vapour sighting. Once digestion was complete the cooled samples were transferred to the distilling unit. The distilled sample was removed for titration. Hydrochloric acid (HCl) was titrated into the sample until it became neutral

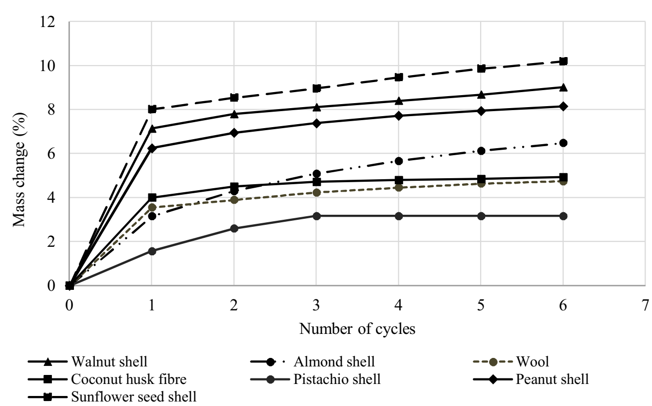

Fig. 1. Shell waste and mass change over 6 cycles.

(clear) with the volume of HCl recorded. The nitrogen content was calculated using Eq. (1):

$$\%N = 14.01x\left(\left(t_s - t_b\right)/m\right)xM_{sd} \quad (1)$$

Where: t_s ml of titration of sample, t_b ml of titration blank, m oven dry weight of sample and M_{sd} molarity of standard HCl (0.01).

3. Results and discussion

Table 2 and Fig. 1 show the maximum formaldehyde absorption by the different shell wastes and wool fibre.

Fig. 1 shows the mass change of each waste shell and wool fibre, over 6 cycles (6 cycles was chosen based on previous experience). The graph reveals there is a rapid mass change in the first cycle and then generally a gradual increase, expect for coconut husk fibre, pistachio shell and wool fibre, which appear to have reached a maximum absorption. The other four shell wastes did not reach equilibrium in the 6 cycles. Theoretical maximum absorption values were determined via regression of the absorption curves for the Almond (65.25 g kg^{-1}), Walnut (92.88 g kg^{-1}), Sunflower (117.313 g kg^{-1}) and Peanut (81.52 g kg^{-1}). The calculated values for almond and peanut are within the standard deviation of the observed values with only the walnut and sunflower giving theoretical values outside the standard deviation of the observed.