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Assessment of lignocellulosic nut wastes as an absorbent for gaseous formaldehyde

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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.

Key words: Nut waste, Dynamic Vapour Sorption, Formaldehyde, Kjeldahl, Absorption

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 (mo 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.

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 tonnes/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 tonnes /year)[5], North America the 2nd (300,000 tonnes/year)[16] and Iran is the 3rd (150,000 tonnes/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 tonnes/year)[7,8]	489,000 tonnes[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 151,00ha 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 tonnes/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 G E, 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]

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.

2. Materials and Methods

2.1 Nut shell Waste and Wool

The shell material was dry and oil free and crushed into small pieces (<3mm) 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 <5mm pieces and removing any contaminating material. The material was then oven dried overnight in a 50^{o}C oven. Between 0.2g and 0.3g of the oven dried waste shell, weighed to four decimal places, and were placed into digestion tubes to which two Kjeldahl peroxide tablets and 12ml of sulphuric acid were added. The digestion tubes were then placed in a preheated (420^{o}C) digester and left to digest for 1 hour 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 (clear) with the volume of HCl recorded. The nitrogen content was calculated using equation 1:

$$\% N = 14.01 \, x \left((t_s - t_b)/m \right) x \, M_{sd} \qquad \text{[Equation 1]}$$

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.

Table 2: Formaldehyde absorption by shell waste and wool fibre and their nitrogen content

Scavenger	Formaldehyde absorption (g kg^{-1})	SD	Nitrogen content (%)	SD
Wool	49.80	0.35	17.16	0.02
Walnut shell	90.19	0.91	1.12	0.22
Almond shell	64.86	0.67	0.26	0.11
Coconut husk fibre	49.29	0.52	0.31	0.00
Pistachio shell	31.70	0.49	0.10	0.01
Peanut shell	81.48	0.43	0.73	0.03
Sunflower seed shell	101.97	0.22	4.17	0.18

Figure 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.

The nitrogen content was analysed to determine if there was a relationship between protein content and formaldehyde absorption. Table 2 also shows the Kjeldahl nitrogen content results of the waste shells and wool fibre. The higher nitrogen content of sunflower seed shell, walnut shell and peanut shell (4.17%, 1.12% and 0.73% respectively) correlates with their higher capacity to absorb formaldehyde (101.97 g kg^{-1}, 90.19 g kg^{-1}and 81.48 g kg^{-1}respectively). However, it appears the wool fibre values do not fit this relationship. Wool has a significantly higher nitrogen content17.16%, as it is of a protein structure, but it absorbed significantly less formaldehyde (49.80 g kg^{-1}), than the top three shell waste scavengers. The Kjeldahl method measures total nitrogen and therefore may detect non protein nitrogen compounds within the wool.

The reactions between formaldehyde and other compounds and molecules is very complex, as formaldehyde has low specificity and will readily react with a number of compounds in different ways (Reddie and Nicholls, 1971). The reactions between wool and formaldehyde are very complex. Polyamides form the backbone of the wool proteins and are comprised of many functional groups, each with varying reactivity (Reddie and Nicholls, 1971). The wool keratin reacts with formaldehyde and formaldehyde irreversibly binds to asparagine amide groups of the wool (Alexander et al., 1951; Middlebrook, 1949).

It is well reported that formaldehyde will react and bind with amino groups and result in the formation of a methylol derivative (Alexander et al., 1951; Levy and Silberman, 1937; Puchtler and Meloan, 1984; Reddie and Nicholls, 1971). Other crosslinks are formed between amine and amide, amine and phenol and amine and indole groups (Alexander et al., 1951). Lignocellulosic wastes composition contain a wide variety of functional groups (Altun and Pehlivan, 2012; Miretzky and Cirelli, 2010; Okuda et al., 2003; Reddie and Nicholls, 1971; Zitouni et al., 2000). The predominant amino acids found in the lignocellulose material varies with species; walnut contains lysine, in almonds cysteine and methionine and peanut threonine and methionine (Venkatachalam and Sathe, 2006). These differences in the type, composition and quantity of the functional groups may be key factors in determining the ability of a material to absorb and bind formaldehyde. Determination of the different types of functional groups on these waste nut shells may help to explain the differences observed in the quantity of formaldehyde absorbed by the shells and wool. Physical factors may also play an important role as there may be differences due to access via diffusion into the materials and due to different quantities of active nitrogen sites.

4. Conclusions

The purpose of this study was to determine if low cost and unutilised waste nut shell could be used in their natural state to absorb formaldehyde. The study reveals that all the 6 shell types can absorb formaldehyde, with pistachio nut shell absorbing the least and sunflower seed shell absorbing the greatest amount. The Kjeldahl results revealed that the amount of formaldehyde absorbed increased as nitrogen content within the shells increased. To conclude, sunflower seed shell, peanut shell, almond and walnut shell biowaste could be better utilised as organic scavengers to absorb formaldehyde from the atmosphere and improve indoor air quality.

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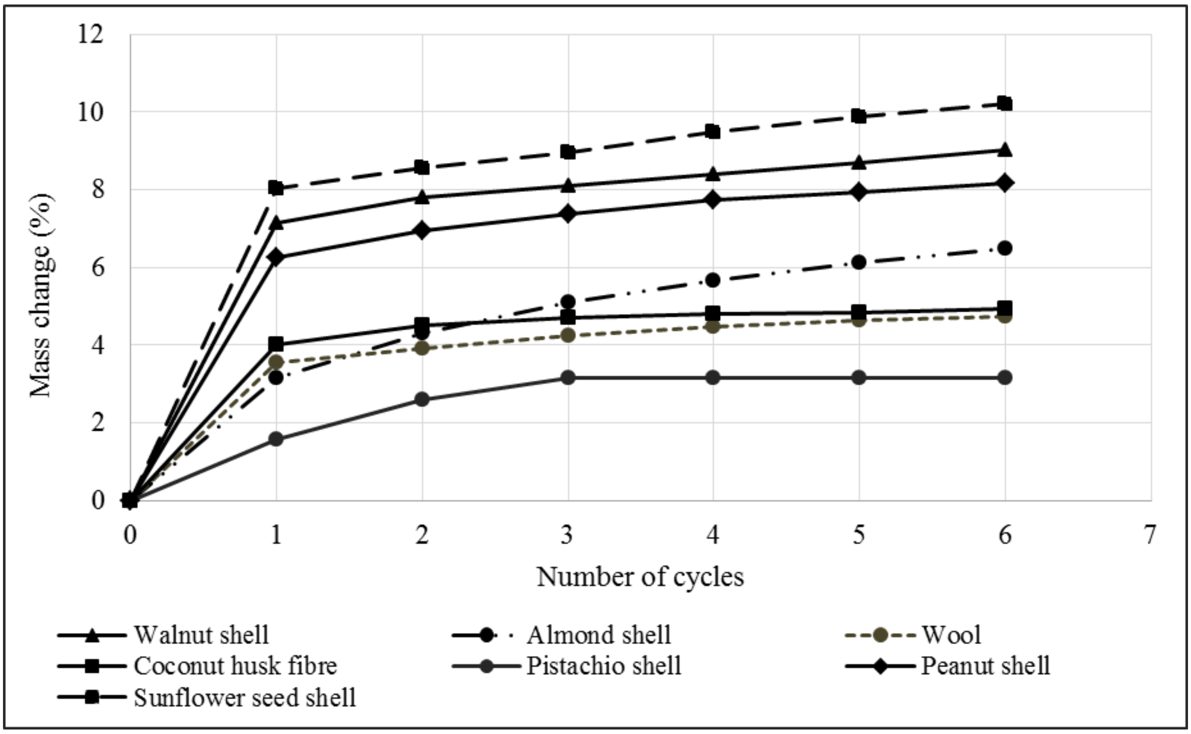

Figure 1: Shell waste and mass change over 6 cycles.