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# Title: Improvement of Indoor Air Quality by MDF panels containing walnut shells

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### Abstract

Poor indoor air quality, including high levels of Volatile Organic Compounds (VOCs) and extremes of Relative Humidity (RH) will negatively affect human health and wellbeing. Materials used in the indoor envelope can act as a sink for airborne pollutants and excess moisture through adsorption. This paper evaluates walnut shell as an additive for MDF board in terms of its ability to regulate RH, toluene, limonene, dodecane and formaldehyde. Adsorption and desorption behaviour of MDF containing 0, 5, 10 and 15 % walnut shell was evaluated in bespoke environmental chambers. The physicochemical properties, including molecular size/shape, molar mass, polarity and boiling point, of the VOC's tested allowed them to represent a range of pollutants. Adsorption and desorption properties were investigated under dynamic conditions at 23 °C and 50 % RH with an air exchange rate of 6 h<sup>-1</sup>. The porous microstructure of MDF panels and the walnut shell surfaces along with the chemical composition were analysed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infra-red spectroscopy (FTIR). Compared to a control panel, walnut shell additions showed an improved ability to remove VOCs and formaldehyde from the indoor air and buffer humidity. Of particular significance was the reduction of airborne formaldehyde concentrations by up to 40 %. This was attributed to the porous surface of walnut shell increasing the specific surface area of the panel and thus its adsorption capacity. This research provides for the first time significant evidence that walnut shell modified MDF can improve indoor air quality. Adoption of this technology will improve human health and reduce diseases caused and exacerbated by poor air quality.

### Keywords

Volatile organic compounds, Indoor Environment, Medium density fibre board, Walnut shell, Indoor air quality, Moisture buffering, Occupant health and wellbeing.

### 1. Introduction

In recent years, there has been a growing concern about poor indoor air quality due to changes in modern building design to conserve energy. The combination of air tightness and high levels of insulation to reduce the heat loss of buildings leads to an accumulation of gas pollutants in the indoor and an increase in Relative Humidity (RH) (Sterling *et al.*, 1985). The optimum

relative humidity levels are between 40% and 60%, with levels outside of this optimum range associated with discomfort, health risks and degradation of some building materials (Fang *et al.*, 1998, Toftum *et al.*, 1998 and Lucas *et al.*, 2002). The World Health Organization estimates that, globally over four million deaths were caused by air pollution in 2012. Gas pollutants, such as Volatile Organic Compounds (VOCs) and formaldehyde, found in an indoor environment can originate from a wide range of sources such as the outdoors, human activities, furniture and building materials, (Da Silva *et al.* 2016a, Crump *et al.* 1997, Dengel 2014, Wolkoff and Nielsen 2001).

The World Health Organization (WHO) classifies VOCs as organic compounds with boiling points from 50 to 260 °C; below 50 °C they are classed as very volatile organic compounds (VVOCs). After a large number of studies on the effects of formaldehyde and VOCs on human health, the WHO guidelines recommend the limit for formaldehyde concentration of 100 mg/m<sup>3</sup>, and across Europe guidelines for total volatile organic compound (TVOC) concentration range from 200 to 500 mg/m<sup>3</sup> within indoor environments, (WHO 2010).

Medium density fibreboard is a well-known formaldehyde emitting material due to the formaldehyde based resin used to bind the wood fibres (Bauman *et al.* 2000, Da Silva *et al.* 2016). Commodity resins contain urea formaldehyde and melamine formaldehyde in their manufacture (Ormondroyd 2015, Ormondroyd and Stefanowski, 2015). In recent years legislation and standardisation has reduced the amounts of formaldehyde that can be released from panel products and this has led to research been undertaken to develop of low formaldehyde emission adhesives and scavengers that can be added to the panel to capture the formaldehyde that would otherwise be released into the environment (Kim 2009, Boran *et al.* 2011, Boran *et al.* 2012, and Pirayesh *et al.* 2013).

Kim (2009) investigated the addition of volcanic pozzolan to the urea-formaldehyde resin to reduce the formaldehyde emission. Pozzolans are usually porous materials composed of siliceous (SiO<sub>2</sub>) and aluminous (Al<sub>2</sub>O<sub>3</sub>) materials (Kim *et al.* 2006). The results confirmed the reduced formaldehyde emissions from the MDF panels with increase of the pozzolan content. The capture of formaldehyde was attributed to the rough and irregular surface, with porous structure, of the pozzolanic materials. Tannin was also added as a formaldehyde scavenger in MDF panels (Boran *et al.* 2012). By adding 1.4 % of tannin solution, the free formaldehyde decreased by 45 %. However, the mechanical properties, such as Modulus of Rupture (MOR) and Internal Bond strength (IB), also decreased with the presence of the tannin. The lower MOR and IB was attributed to the modified fibre structure due to the presence of tannin.

Recently, work has been undertaken to ‘tune’ the properties of the wood fibres by altering the refiner parameters. By changing the refiner pressures Ormondroyd *et al.* (2016) have shown that the porosity, water sorption and surface energy characteristics can be altered and this can lead to less resin required for panel manufacture and therefore less emissions. In further work Ormondroyd *et al.* (2017) assessed the effects of changing the refiner pressure on the ability of the fibre to bond with formaldehyde, it was shown that an optimised refiner pressure can lead to an increase in the absorption of formaldehyde by the fibres.

In Iran, walnut and almond shells are considered as agricultural by-products with no significant industrial usage and as a result they are often incinerated or dumped. Pirayesh *et al.* (2013) studied the formaldehyde emission effect of walnut and almond shell addition to particleboards. When 10, 20, 30 and 100 % of shell was added, results showed that the presence of the shells decreased the formaldehyde emission by 42.8 %. The authors attributed the reduction of the formaldehyde emission to the high amounts of extractives in the shells, and therefore the

presence of large number of polar hydroxyl and phenolic groups. Wood panels could be produced with up to 20 % of walnut shell particles without falling below the minimum EN standard requirements of mechanical properties for general purpose use (Pirayesh *et al.*, 2012).

This paper demonstrates the potential of MDF modified with walnut shell to improve IAQ. MDF panels with 5, 10 and 15 % walnut shell incorporated were compared to a control sample with no shell. VOCs, formaldehyde and moisture adsorption/desorption properties were quantified. An additional the microstructure of the modified panels was investigated. The relationship between physical properties that result in improved IAQ was demonstrated.

## 2. Materials and Methodology

### 2.1. Materials manufacturing

MDF panels were made to a density of 760 kg/m<sup>3</sup>, with area dimensions of 0.4 x 0.4 m<sup>2</sup> and a thickness of 12 mm. The resin loading was 14 % of urea formaldehyde (UF). A commercial mix of spruce, pine and fir chips was refined at 8 bar at the BioComposites Centre, Technology Transfer Centre following the protocols described in Skinner *et al.* (2016). The fibre, scavenger and resin were individually weighed and combined in a drum blender. The resinated fibre was weighed out again and formed into a mat which was subsequently pre-pressed by hand before finally being pressed between two heated platens at 200 °C for 5 minutes following the BioComposites Centre’s standard press profile (controlled by the Pressman control program). The scavenger loading for the panels was 5, 10 and 15% of fibre weight, Table 1.

Table 1. % of walnut addition to MDF fibre.

<b>%</b>	<b>Walnut weight (kg)</b>	<b>MDF fibre (kg)</b>
<b>0</b>	0	1.61
<b>5</b>	0.07	1.27
<b>10</b>	0.13	1.20
<b>15</b>	0.20	1.14

### 2.2. Experimental Methods

The primary aim of this study is to investigate the improvement of IAQ by the addition of walnut shells to MDF. In addition to the adsorption and desorption of VOC measurements, chemical composition and physical and emission properties were also determined. All the tests were conducted in triplicate 28 days after casting, with all specimens stored at 23 °C and 50 % RH.

#### 2.2.1 Material physical and chemical characterisation

The porous microstructures of the specimen panels were analysed by Scanning Electron Microscopy (SEM) with an acceleration potential of 10kV. Squared sections of each material (10 mm x 10 mm) were cut and fixed to an aluminium sample holder with carbon tape. Prior to the analysis, all samples were sputter-coated with a gold-palladium alloy to increase the electrical conductivity and reduce surface charging. This technique allowed the wood fibre and walnut shell particle size and shape to be determined. It was also possible to observe the dispersion of the walnut shell in the MDF 2-dimensional matrix. High magnifications, above x2000, were used to analyse the walnut shell surface.

To assess the chemical composition of the MDF panels a *Perkin-Elmer Frontier* FTIR spectrometer equipped with a *MIRacle™ Single Reflection ATR* (attenuated total reflectance) with diamond crystal from PIKE technologies was used. The IR spectroscopy was carried out

over a wavelength range from 600 to 4000  $\text{cm}^{-1}$ , with 2  $\text{cm}^{-1}$  of resolution, 25 scans of accumulation and 0.5  $\text{cm/s}$  of scan speed. Three spectra were recorded in different zones to validate the data. X-ray diffraction was conducted using a *Bruker-AXS D8* powder X-ray diffractometer operated at 40 kV, 40 mA with a Cu-K $\alpha$  X-ray source and  $\lambda = 1.5405 \text{ \AA}$ . The sweeping angles ( $2\theta$ ) used were between 5 and 80° with a step size of 0.016° at ambient temperature. NIST chemistry Webbook for organic based materials was used as a library for peak identification for both FTIR and XRD results (Linstrom and Mallard 2011).

### 2.2.2. Rig for emissions and adsorption and desorption curves of VOCs and formaldehyde

To evaluate the environmental performance of the MDF panels incorporating walnut shell in terms of improving the indoor air quality, adsorption/desorption testing was carried out by exposing the samples to a mixture of formaldehyde, toluene, limonene and dodecane in air. The adsorption and desorption investigations was performed in 2-litre environmental chambers in accordance with BS ISO 16000-9 and BS ISO 16000-24. Figure 1 shows a schematic diagram of the rig used to supply air containing VOC's to the 2-litre chamber. It consists of a number of connected components including a pure air generator, chambers containing VOCs and formaldehyde sources, and the 2-litre environmental chambers in which the testing materials are placed. The rig has the capacity to test several materials simultaneously in individual chambers and to run one reference chamber (containing no material) for comparison. Valves placed before the chambers allow the flow of either pure air or dopant air (a mixture of toluene, limonene, dodecane and formaldehyde in air) into the chambers.

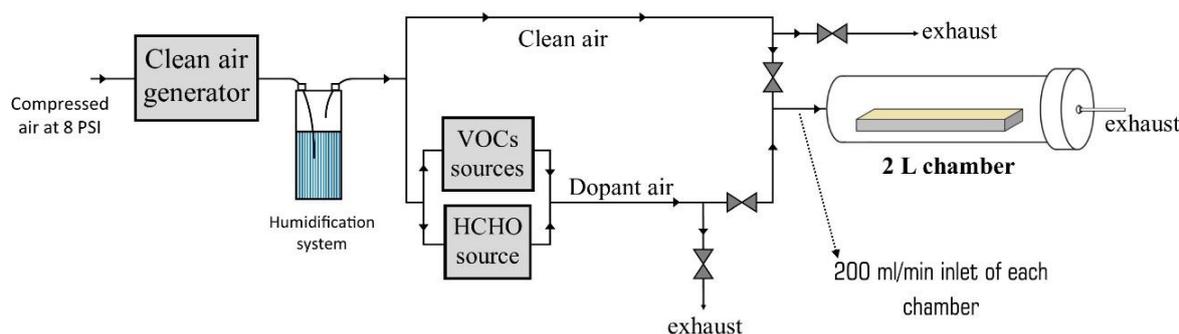


Figure 1. Experimental rig for measuring the adsorption and desorption of VOCs formaldehyde by the wood panels with walnut shell.

The experiments were carried out under controlled temperature and relative humidity, 23 °C  $\pm$  2 °C and 50 %  $\pm$  5 %. Mass flow controllers were placed after the pure air generator to adjust the flow rate of VOCs and formaldehyde sources and the pure air flowing directly to the 2-litre environmental chambers. The inlet flow rate of gas entering the 2-litre chambers was maintained at 200 ml/min (equivalent to an air change rate of 6  $\text{h}^{-1}$ ). All tubes, valves and joints used in the rig assembly were made of emission-free and non-adsorbing materials.

MDF panels were cut into samples with nominal dimensions of 200 mm  $\times$  60 mm  $\times$  15 mm and enclosed in an emission-free boat, so that adsorption/desorption mechanisms could occur only from the exposed surface area. Prior to the adsorption/desorption experiment, the testing materials were conditioned inside the environmental chambers for more than 28 days under a flow of pure air. During this period, VOCs and formaldehyde emissions were analysed to identify the presence of emissions that could affect the adsorption/desorption study.

The sampling and analytical procedures for VOCs and formaldehyde were made in accordance with the standards BS ISO 16000-6 and BS EN ISO 16000-3, respectively. Air sampling of VOCs was undertaken in the exhaust of the chambers by using Tenax TA tubes with a flow rate of 150 ml/min for 10 min. The qualitative and quantitative analysis of VOCs was carried out in an ATD-GC/MS (*Perkin-Elmer*) fitted with a FID detector. Formaldehyde sampling was carried out by using Sep-Pak 2,4-DNPH cartridges at the same flow rate and duration of VOC sampling. After solvent desorption from the 2,4-DNPH cartridges using acetonitrile, the formaldehyde solutions were analysed by HPLC (*Gilson*). Quality control samples of VOCs and formaldehyde were run prior to all analyses. VOCs and formaldehyde samples were taken at:

- Adsorption – 0, 1, 2, 4, 24, 48, 144, 218 and 285 hours;
- Desorption – 1, 2, 5, 24 and 48 hours.

In Table 2 the physicochemical properties of formaldehyde, toluene, limonene and dodecane are presented.

Table 2. Physicochemical properties of formaldehyde and selected VOCs.

	<b>Formaldehyde</b>	<b>Toluene</b>	<b>Limonene</b>	<b>Dodecane</b>
<b>Formula</b>	CH <sub>2</sub> O	C <sub>7</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>12</sub> H <sub>26</sub>
<b>Chemical conformation</b>	Simple	Aromatic	Cyclic	Straight chain
<b>Polarity</b>	Polar	Non-polar	Non-polar	Non-polar
<b>Molar mass (g/mol)</b>	30	92	136	170
<b>Boiling point (°C)</b>	-19	111	176	216

The four organic compounds selected represent a range of molar masses and physicochemical characteristics of VOC's typically found within indoor environments. Formaldehyde is considered a very-VOC (VVOC) due to its very low boiling point and is of particular importance as it is often found in indoor environments and can cause severe health effects (WHO 2010).

### 2.2.3. Moisture buffering

The moisture buffering test was conducted using ISO 24353:2008 using the mid-level humidity cyclic test method. This method required specimens to be pre-conditioned at a relative humidity of 63 % and a temperature of 23 °C before cyclic climatic variations were started. Four cycles of the following conditions were run whilst the mass of the specimen was logged:

- Step 1: 12 h, relative humidity of 75 % and temperature of 23 °C;
- Step 2: 12 h, relative humidity of 50 % and temperature of 23 °C.

Specimens were cut to 100 mm x 100 mm and aluminium tape was used to seal the back and sides of these specimens to ensure vapour exchange only occurred through a single face of the material. These were then tested using environmental chambers programmed to subject the specimens to the humidity cycles set out above. Mass balances installed inside the chambers were used to record specimen mass at 5 minute intervals. A screen was placed around the mass balance to minimize the influence of air movement over the surface of the specimens during testing. An anemometer was used to measure wind speed at the specimen surface and was found to be an average of 0.1 m/s. Fourth cycle moisture adsorption and desorption content values and rates were calculated in accordance with Section 8.3 of ISO 24353:2008.

## 3. Results and discussion

### 3.1. Microstructure

Scanning electron microscope images of the MDF panels with walnut shell are presented in Figures 2 a) to d). MDF panels were manufactured to achieve a density as close to  $760 \text{ kg/m}^3$  as possible. It became apparent however that packaging of the wood fibres in the MDF panels with higher contents of walnut shell led to a more compact structure than expected. This resulted in the voids between each single wood fibre in the MDF matrix being smaller for the panels with higher contents of walnut shell which led to a higher surface area, Figure 2 d). Figure 3 shows the walnut shell particles embedded in the MDF matrix.

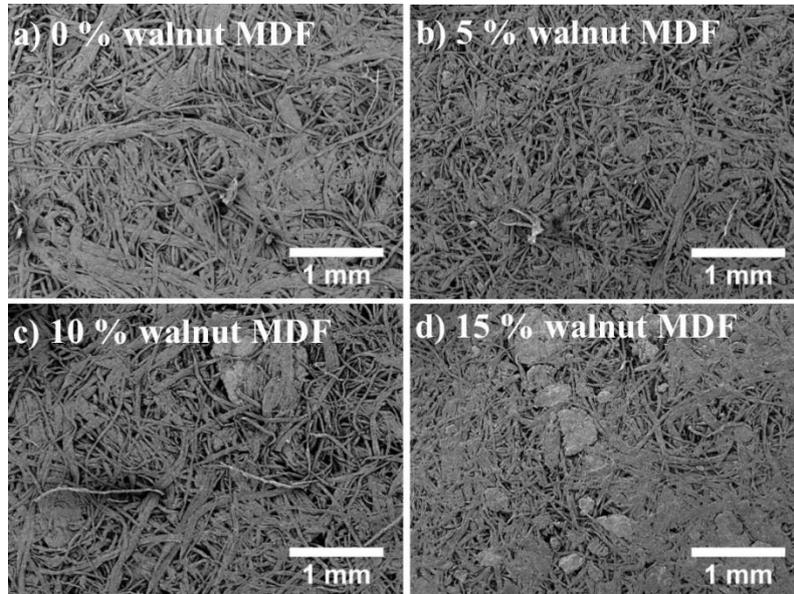


Figure 2. Scanning electron microscopy images of a), b), c) and d) MDF panels with walnut shell at x30 of magnification

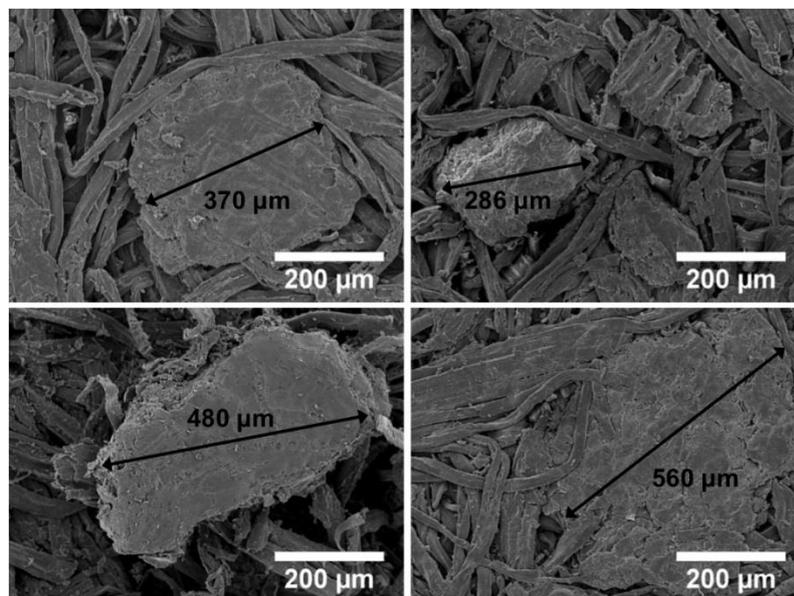


Figure 3. A number of representative scanning electron microscopy images of walnut shell particles of varying size.

Macroscopically, walnut shell does not show porosity as seen in Figure 3 although, at higher magnifications a highly porous structure can be observed, Figure 4 a) and b). The wood fibre surface is shown in Figure 4 c) and d). The average size of the pits in the wood fibre is 670 nm.

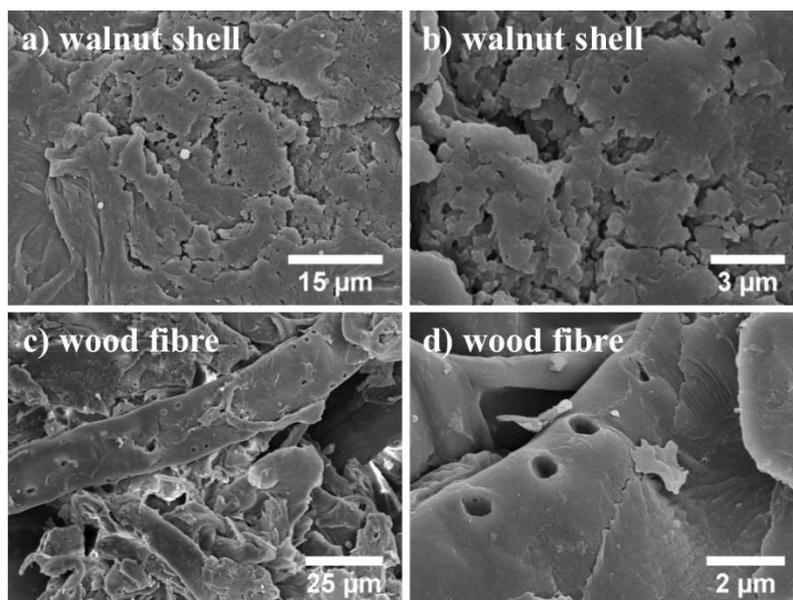


Figure 4. Scanning electron microscopy images of a) and b) the walnut surface, c) and d) MDF wood fibre surface.

Walnut shell presents an irregular porous surface with pore sizes ranging from 25 nm to 1224 nm. The pore size of the walnut shell was measured using ImageJ version 1.48 image analysis software. An average pore size of 330 nm was obtained from a sample of two hundred measurements. As the pore size distribution is wide the average is not representative and thus it is plotted as a size distribution, Figure 5. In a sample of 200 pore size measurements, 20 % of the pores exhibited sizes between 25 and 74 nm. Overall, 65 % of all measured pores showed sizes below 374 nm.

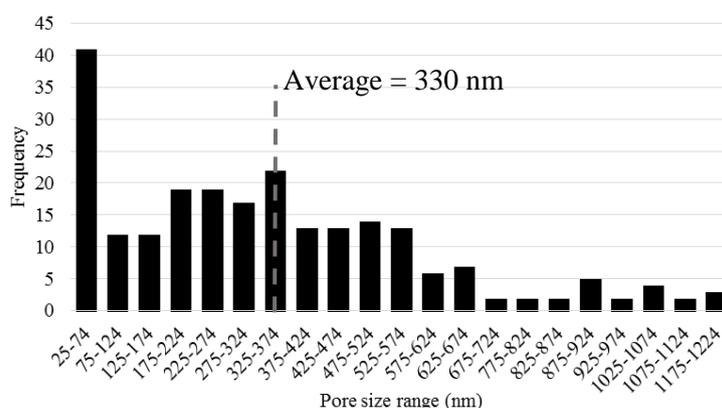


Figure 5. Pore size distribution of the walnut shell.

In Figure 6, an FTIR spectrum and X-ray diffractogram of the reference MDF panel (no added walnut) are shown. Characteristic bands for cellulose, hemicellulose and lignin were identified in the FTIR spectrum. Stretching vibrations of hydroxyl groups present in the cellulose molecule such as  $-\text{CH}-\text{OH}$  and  $-\text{CH}_2-\text{OH}$  are shown in the  $3400$  to  $3300 \text{ cm}^{-1}$  wavelength range. Stretches of  $-\text{CH}$  and  $-\text{CH}_2$  groups occur at  $2918$  and  $2852 \text{ cm}^{-1}$  range. The surface  $-\text{OH}$  bending vibrations are verified around  $1645 \text{ cm}^{-1}$ . The range from  $1500$  to  $1200 \text{ cm}^{-1}$  relates the primary and secondary hydroxyl bending and the  $\text{C}-\text{O}$  stretching vibration is observed at  $1261$ - $1028 \text{ cm}^{-1}$ . In the X-ray diffractogram, Figure 6 b), two peaks from the semi-crystalline cellulose are shown at  $2\theta$  values of  $16$  and  $23^\circ$ .

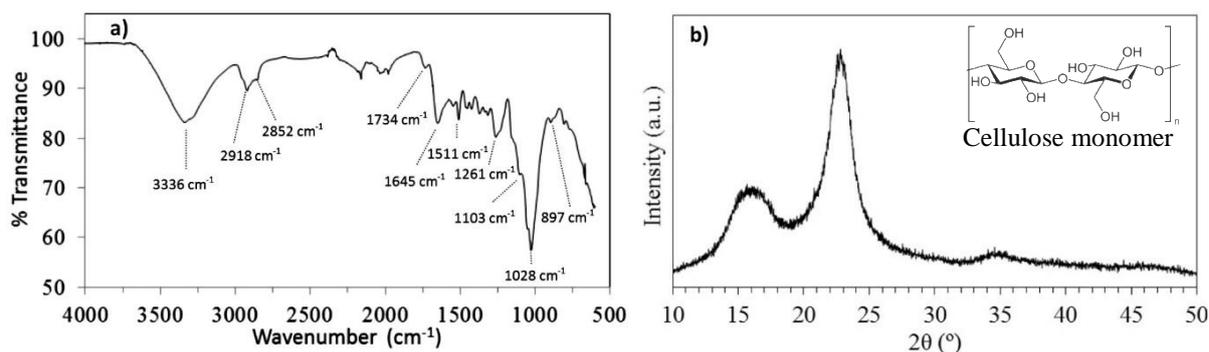


Figure 6. a) FTIR spectrum and b) X-ray diffractogram of MDF.

### 3.2. VOCs and formaldehyde emissions

Emissions tests were carried out by passing only pure air through the chambers. Air in the exhaust of the chambers was sampled after 3 and 28 days as per BS EN ISO 16000-9:2006. The concentration of formaldehyde and total-VOCs in the chamber was then calculated as the area specific emission rate ( $\mu\text{g m}^{-2} \text{h}^{-1}$ ), Figure 7.

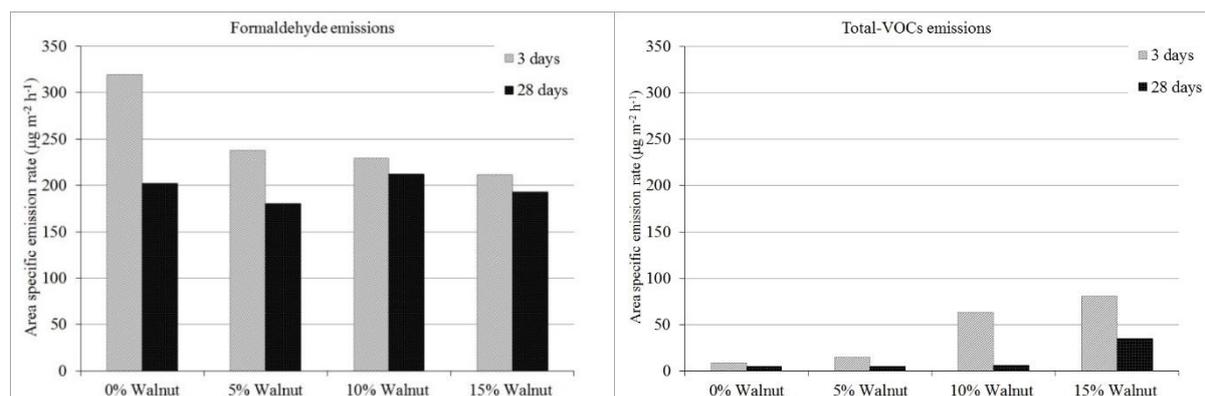


Figure 7. Area specific emission rate of formaldehyde total-VOCs from the wood panels. Major VOCs emitted: acetic acid and 2-ethylhexane-1-ol.

Formaldehyde emission rate was lowest for the MDF panel with 15 % walnut shell content. In comparison the MDF panel with the highest walnut content emitted 34 % less formaldehyde than the MDF without walnut. Pirayesh *et al.* (2013) also observed a decrease in formaldehyde released by the particleboard with higher walnut content using the BS EN 717-3 standard methodology. Similar observations were reported in other studies (Ayrilmis *et al.* 2009 and Boran *et al.* 2012). In an adsorption process two types of interactions can occur between the solid and fluid phase: physisorption and chemisorption (Rouquerol *et al.* 1999). The chemical nature of the material and its physical characteristics (*e.g.* open porosity, pore size distribution *etc.*) will determine if the interaction between the material surface and the organic pollutants is physical, chemical or even a combination of both, (Da Silva *et al.* 2016a and Da Silva *et al.* 2016b). Da Silva *et al.* (2016a, 2016b) suggested that interactions between building materials and organic pollutants are a combination of physical and chemical processes. Materials such as cellulose from the wood fibres which have high surface area and chemical components with negative/positive charges or hydroxyl groups typically exhibit a combination of physisorption and chemisorption when exposed to organic pollutants. In the case of MDF panels, the reduction of formaldehyde emissions with the increase in walnut shell content can be attributed

to the porous microstructure of shell surface leading to a higher specific surface area and hydroxyl groups present in the chemical components of the material as discussed previously.

### 3.3. VOCs and formaldehyde adsorption/desorption

The adsorption and desorption behaviour of MDF panels with walnut shell are shown in Figure 8. Adsorption/desorption curves represent the concentration of formaldehyde and VOCs in the chambers of each material plotted over the elapsed time. The difference of concentrations in the reference chamber and a chamber containing a material is the amount of VOC adsorbed on to the material surface.

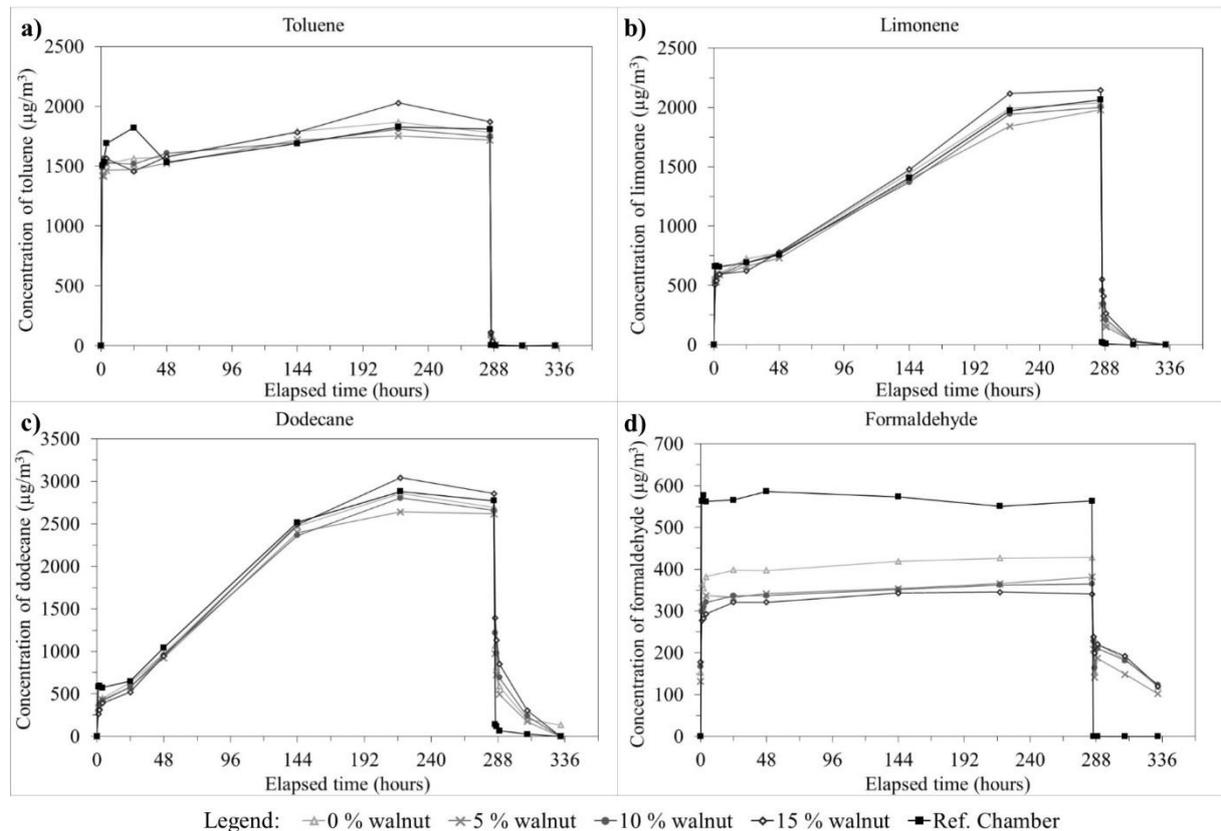


Figure 8. Adsorption/desorption curves of a) toluene, b) limonene, c) dodecane and d) formaldehyde.

Considering the adsorption and desorption behaviour of all samples with respect to the four pollutants, toluene was the least adsorbed volatile compound and formaldehyde was the most. This indicates that less polar molecules have a lower affinity for adsorption compared to those with higher polarity such as formaldehyde. Aromatic and cyclic compounds, including toluene and limonene, were the least adsorbed. Similar observations were made by Da Silva *et al.* (2016a), Mansour *et al.* (2016) and Niedermayer *et al.* (2013). Dodecane was more preferentially adsorbed compared to toluene and limonene because its molecule structure is a linear hydrocarbon chain, allowing it to be flexible and able to curl and bend facilitating the diffusion through pores and capillaries of the walnut shell and wood fibre. During desorption no toluene was detected in any chamber after five hours from the start of this phase. At 48 hours, dodecane and formaldehyde were still being desorbed by the materials.

The adsorption (up to 24 hours) and desorption (up to the end of the experiment) behaviour of formaldehyde by the MDF panels is shown in Figure 9.

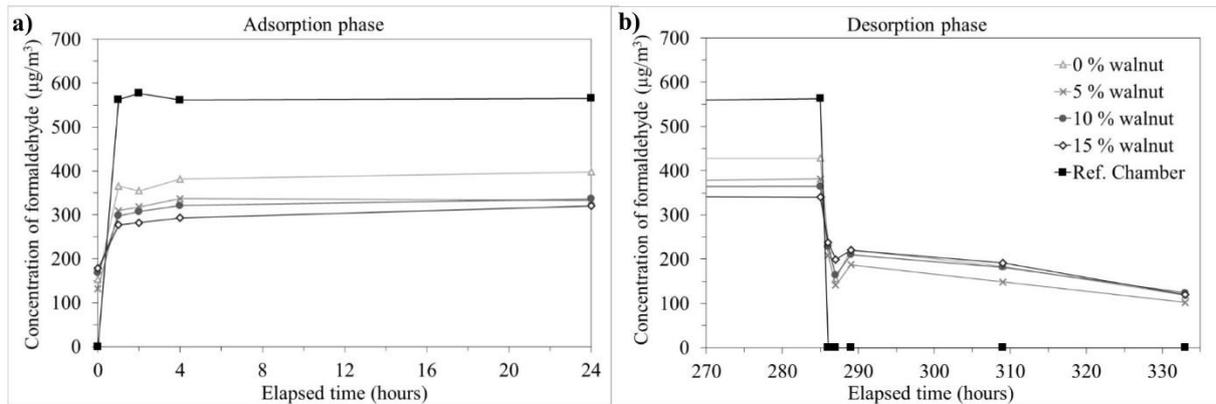


Figure 9. a) Adsorption curve of formaldehyde in detail and b) desorption curves of formaldehyde in detail by the wood panels with walnut.

Figure 9 a) shows the concentration of formaldehyde reached its maximum in the reference chamber after one hour and remained almost constant until the end of the adsorption phase at 285 hours. During the desorption phase, figure 9 b), the concentration of formaldehyde dropped immediately to 0  $\mu\text{g}/\text{m}^3$  in the reference chamber. Interestingly the MDF containing 15 % walnut exhibited the lowest concentration of formaldehyde during the adsorption phase, figure 9 a), indicating that walnut shell has a strong adsorption efficiency with regard to formaldehyde. A small perturbation at the beginning of the desorption phase, at 285 hours, is visible in figure 9 b). For all samples the formaldehyde concentration in the chamber dropped to a minimum at 287 hours before increasing again to a slightly higher value at 290 hours. This behaviour is consistent with two desorption processes taking place on/in the sample surface over these first few hours of desorption. It is beyond the scope of this investigation to confirm the exact nature of these, however it could be hypothesised that a proportion of the formaldehyde is surface adsorbed and can be released quickly into the pure air atmosphere. In addition, there may be formaldehyde present in the sub-surface pore network of the sample which must negotiate a diffusion path before final release into the chamber atmosphere, which would take more time. This behaviour may be a consequence of the difference in chemical and physical properties of the wood fibre and walnut shell phases present in the test specimens.

The amounts of formaldehyde adsorbed (%) by the MDF panels after 285 hours is shown in Figure 10. For this, the difference between the concentrations in the reference chamber and in the material containing chambers was calculated as a percentage. Formaldehyde concentration in the reference chamber was considered to be 100 %.

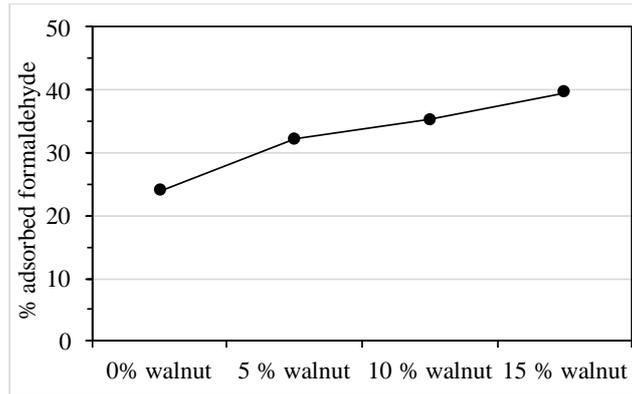


Figure 10. % of formaldehyde adsorbed by MDF panels with walnut shell at 285 hours elapsed time.

The MDF panel with 15 % walnut reduced the formaldehyde concentration in the chamber by 40 %. In contrast, the reference MDF (no walnut added) adsorbed 24 % of the formaldehyde. The results show that by adding 15 % of walnut to the MDF matrix the formaldehyde uptake is almost doubled, increasing from 24 to 40 %.

### 3.3. Moisture buffering

The moisture adsorption and desorption characteristics of the MDF control specimen (0% walnut) and specimens with 5, 10 and 15% walnut shell are presented in Figure 11. Three specimens of each variation type were tested and the error bars represent the 95% confidence interval. Although an alternative method was used, the results can be compared against classifications for moisture buffering of materials proposed by Rode *et al.* (2005). The MDF panel without any modification would be classified as *good*. Panels containing 10% and 15% walnut shell exhibited improvements of 34% and 44% respectively, leading to a moisture buffering material classification of *excellent*.

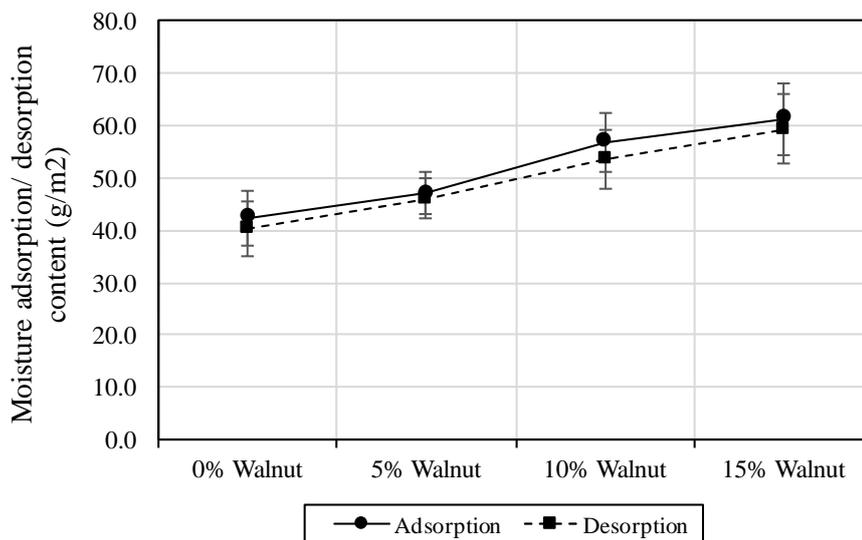


Figure 11. Moisture adsorbed by MDF panels with walnut shell.

## 4. Summary and conclusions

This study demonstrates the ability of MDF panels containing walnut shell to improve the indoor air quality. This achieved through lower initial emissions, removal of organic pollutants, and improved moisture buffering properties. MDF panels with higher walnut shell contents

showed a greater ability to adsorb organic pollutants and moisture. Polar compounds, such as formaldehyde and water, and compounds with linear molecular chains, such as dodecane, were adsorbed more readily by all materials when compared with the cyclic compounds such as toluene and limonene. The removal of pollutants from the air was observed not only during the adsorption/desorption tests but also during the emissions testing. The incorporation of walnut within the MDF panels showed excellent promise for the future of MDF as a building material. This is particularly important as MDF has been identified as a problematic material due to its high formaldehyde emissions. In particular this negatively impacts on the health and wellbeing of humans exposed. Adoption of walnut shell as an additive in fibre-based building materials will not only improve indoor air quality, but also provide an alternative to landfill or incineration of the shell, with an associated reduction in embodied CO<sub>2</sub>.

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