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Nutrient removal capacity of wood residues for the Agro-environmental safety of ground and surface waters

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Abstract

The aim of this study was to determine the effectiveness of wood residues in the removal of nutrients (ammonium-N; NH_4-N) from nutrient-rich (NH_4-N) waters. The water holding capacity of the wood materials was also determined. Carried out at Rothamsted Research, North Wyke, UK, this controlled laboratory experiment tested two wood residues; in length, one being 1-2cm and the other from 150 µm (microns) to 9.5mm. Although a wide range of studies have shown the effectiveness and performance of various absorbent materials as animal beddings, such as straw (cereal straw), woodchip (sawdust, bark or wood shavings), bracken and rushes, only few have focused on the NH_4-N sorption/desorption capacity.

The depuration capacity of wood residues from nutrient-rich effluents such as those from cattle bedded on woodchip or straw will be controlled by processes such as sorption (adsorption-absorption) and desorption of nutrients. Studies have reported the nitrogen removal capacity of woodchip materials and biochar from woodchip as well as removal of NH_4^+-N from domestic and municipal wastewater, farm dirty water, landfill and industry effluents. These studies have observed that the mechanism of removal of nitrogen is by either increasing NO_3^--N removal form leachate by enhancing N_2O losses via denitrification (biochar as carbon source for denitrifiers) or by decreasing NH_4^+-N in leachate through adsorption to negatively charged sites.

Results showed that although the cation exchange capacity (CEC) and surface area (SA) are both fundamental properties of adsorbent materials, no correlation was found with CEC and adsorption or desorption. Nor did changes in pH appear to be sufficiently important to cause changes in CEC. For this reason, osmotic pressure appeared to be a more predominant parameter controlling processes of adsorption and desorption of NH_4^+-N in both wood residues. Thus, wood residues high in NH_4^+-N should be avoided, as they could have an opposite effect in the adsorption of nutrients from nutrient-rich effluents.

The results also showed that some wood residues (G30) had great capacity to adsorb NH_4^+-N to levels up to nearly 90% whilst demonstrating low desorption capacity of NH_4^+-N (less than 1%). These are ideal relevant features for an adsorbent material for the removal of nutrients (or heavy metals) from contaminated waters such us farm o industrial effluents, or for the depuration of eutrophic watercourses. This could help reduce the concentration of farm effluents making them more manageable, subsequently contributing towards the compliance of new environmental regulations.

Keywords: nutrients, nitrogen, ground and surface water

Introduction

Several studies have been carried out to better understand the water holding capacity (WHC) of various adsorbent materials (Beardsell et al., 1979; Himelick & Watson, 1990; Goto & Yokoe, 1996; Taleisnik et al., 1999; Davis & Wilson, 2005; Luo & Lindsey, 2006) though most of these experiments were aimed to look at their significance as soil amendments. Other studies have observed the effectiveness and performance of various absorbent materials as animal beddings, such as straw (cereal straw), woodchip (sawdust, bark or wood shavings), bracken and rushes (Schofield, 1988; Deininger et al., 2000; Ward et al., 2000; Ward et al., 2001; Luo et al., 2006; Vinten et al., 2006; Molnar & Wright, 2006). But the list of absorbent materials is variable. In other countries, for example, green cuttings, farm-hedge trimmings, waste shredded newspaper, chopped cardboard, plasterboard backing paper, zeolite, shredded bricks, shredded chestnuts, coir, pea haulm, oilseed rape straw, canary reed grass, miscanthus and peat moss, are also widely used (Ward et al., 2001; Pohl, 2002; HCC, 2010; Logan, 2011).

The cation exchange capacity (CEC) and surface area (SA) are both fundamental properties of adsorbent materials because together they control the capacity to hold water and nutrients; the greater the SA and CEC, the greater the WHC (Harada & Inoko, 1980; Chiou et al., 1990; Ragland et al., 1991). The CEC indicates the number of negatively charged binding sites in the surface of the adsorbent material that are available to bind positively charged ions, also referred to as nutrient holding capacity (Kitsopoulos, 1999; Camberato, 2001; Yara, 2012). The surface area is calculated using the BET (Brunauer, Emmett and Teller) method (Brunauer et al., 1938) and refers to the surface that is accessible to the molecules -of any particular gas or liquid- being sorbed (Love & Whittaker, 1954). The higher the CEC and surface area are of any particular material, the greater will be the capacity to adsorb positively charged ions (Shukla et al., 2002).

The quality of the effluent from cattle bedded on woodchip will also be controlled by processes such as sorption (adsorption-absorption) and desorption of nutrients as well as other factors (e.g. woodchip type, pad design, feeding management) (O'Driscoll et al., 2007). Studies have reported the nitrogen removal capacity of woodchip materials and biochar from woodchip (Burn & Mason, 2005; Luo et al., 2006; Pagans et al., 2007; Ruane et al., 2010), as well as removal of ammonium-N (NH_4^+-N) (Lens et al., 1994; Clabaugh, 2001; Galera et al., 2008; Sironi et al., 2009; Christianson et al., 2011) from domestic and municipal wastewater, farm dirty water, landfill and industry effluents. These studies observed their removal capacity by either increasing NO_3^--N removal form leachate by enhancing N_2O losses via denitrification (biochar as carbon source for denitrifiers) or by decreasing NH_4^+-N in leachate through adsorption to negatively charged sites. However, not much research has been undertaken to study adsorption and desorption of NH_4^+-N by fresh woodchip materials (Airaksinen et al., 2001; Bolan et al., 2004). Bolan et al (2004) state that NH_4^+-N retention by bark (Pinus radiata) is strongly related to increases in the CEC of the woodchip material. The authors also observed that microbial immobilisation plays and important role in the retention of nitrogen.

Airaksinen et al (2001) found that the ammonia adsorption capacity of woodchip submerged for two hours in fresh horse urine at 17.5^oC was 44% of initial ammonia content (not specified by the author), and that the ammonia adsorption capacity by woodchip would be expected to increase with rises in indoor housing temperatures. In other studies, a natural zeolite material (synthesised from South African coal fly ash) has shown to have the capacity to remove Cr, Cd, Cu, Pb, Zn and Ni from heavy metal-contaminated waters by up to 99 to 100% within the first two hours of submersion, for all metals (Koukouzas et al., 2010). In a lysimeter experiment, Luo et al (2006) studied the effect of soil, bark, woodchip and zeolite in reducing drainage N losses from periodically applied cattle excreta. The author found that woodchip could retain c.35% of the applied excretal nitrogen and that NH_4^+-N was the most common form of nitrogen present in the drainage across all the experimental materials.

A study on experimental corrals found that the particle size of woodchip and the depth had no effect in the amount of nitrogen retained by this material (Vinten et al., 2006). On a similar study, Luo et al (2008) determined that sawdust and bark (from Pinus radiata) had no effect on nitrogen retention when used as bedding for dairy cows, and contrary to the finding of the former author, both woodchip media retained 96% of deposited excretal N and therefore nitrogen losses through leachate were minimal.

The objective of this study was to determine the capacity of two woodchip materials to adsorb and desorb variable concentrations of NH_4^+-N solutions, as well as their water-holding capacity.

Materials and methods

This study was carried out, under controlled laboratory conditions, at the Sustainable Soils and Grassland Systems Department, Rothamsted Research, North Wyke, Okehampton, Devon, United Kingdom.

Woodchip size and type. Two woodchip types were used for this experiment; the first is commercially named G30 measuring 1-2 cm in length and conforming dice-shape woodchips. The second woodchip was sawdust, manufactured from shredded pallet material, measuring 150 µm to 9.5 mm in length (Figure 1).

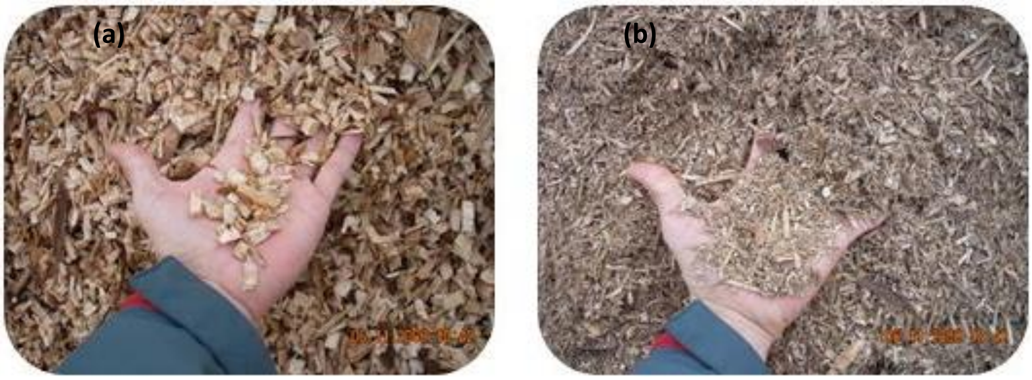

Figure 1. Wood residues tested as materials for the removal of nutrients from nutrient-rich effluents. G30 (a), 1-2 cm in length. Sawdust (b), 150 µm to 9.5 mm in length.

The source for G30 was round-wood Douglas fir timber (Pseudotsuga menziesii) chipped and piled on site by an outside supplier. Sawdust was bulked delivered by a different provider. Approximately 20kg of each woodchip type was collected directly from each pile and stored hermitically at 4^{o}C, in 50-litre barrels.

Physical and chemical properties of both woodchip materials

Initial water content (IWC). The IWC of each woodchip was determined by placing c.3kg of fresh-moist sample into an aluminium tray (of previously recorded weight) and its fresh weight recorded before drying in an oven at 105^{o}C for 36 hours. Samples were then removed from the oven and the dry weight recorded (a) and subtracted from the fresh weight to obtain water content (b). The IWC was then calculated by the formula described below and expressed as a percentage of its dry weight (e.g. 100g of moist woodchip, weighing 40g when dry (a) contain 60g of water (b), have 150% IWC): WC = (b / a)*100.

Woodchip density (WD). In a replicated way, a container of known volume (a) was filled entirely with each fresh woodchip type and weighed (b). Woodchip density was determined as WD = (b / a) expressed in grams per cubic centimetre (g cm^{-3}) or kilos per cubic metre (kg m^{-3}), fresh weight basis.

Particle size characterisation. Particle size was determined separately for each woodchip type. In a replicated way c.30g of dry sawdust and G30 were passed through different calibrated sieves to categorise the particles into groups. Sawdust particles were passed through sieves measuring 9.5-4.0 mm, 4.0-2.0 mm, 2.0-1.0 mm, 1.0-0.5 mm and 500-150 µm while for G30, particles were passed through sieves of 20.0-9.5 mm, 9.5-4.0 mm, 4.0-2.0 mm, and 2.0-1.0 mm. Each particle-size group was weighed after sieving to determine the proportion of bulk weight.

Water holding capacity (WHC). To determine WHC, 30g (±0.1g) of dry woodchip (b) of each type was placed into a 500 ml plastic bottle and 200ml of deionised water was added, to insure sufficient availability of water for the woodchip to hold. Samples were then hand shaken and kept at 4°C prior to sampling. WHC was measured at T0, T30min, T1h, T3h, T6h, T1d, T3d, T7d, T14d, T30d, T45d, and T60d. At each sampling occasion, the non-retained water from each bottle was removed using a perforated lid to reduce losses of woodchip through suspended material. Then the remaining woodchip was weighed (a) directly from the bottle (bottles had a standard known weight with variations of ±0.5g) and its WHC determined using the following formula, and expressed as a percentage of its dry weight:WHC = ((a – b)/b)*100.

Dry matter content was also determined under the same method, but expressed as percentage of moist weight. The sampling interval measured at T0 (entrained) was to determine the capacity of woodchip to entrain water in its matrix. Samples were shaken by hand to insure good mixing with the woodchip, and the whole content of water discharged instantly after mixing, hence to avoid water being adsorbed.

Cation exchange capacity (CEC). Values for CEC for Sawdust and G30 were obtained from Darch (2009) who reported mean values of 14.3 and 7.4 mmol/100g, respectively, on studies on the same woodchip materials described in this experiment.

Surface area (SA). Surface area was not determined in this experiment; however, studies in the literature show a wide variability in wood (wood pulp or ground wood) that ranges from 5 to 40m^2 g^{-1}using the BET standard (Gordon, 1963; Stone & Scallan, 1965; Elalem, 2010). Furthermore, a value of 143 m^2 g^{-1} was reported by Habib-ur-Rehman et al (2006) on sawdust of Dalbergia sissoo, but using the Snow’s iodine adsorption method (Studebaker, 1957).

Ammonium adsorption and desorption measurements. Ammonium adsorption and desorption was determined by putting c.30g (±0.1g) of each woodchip type into a 500ml plastic bottle where 200ml of corresponding NH_4^+-N concentrations were added. These ammonium concentrations were previously prepared in the laboratory using ammonium chloride (NH_4Cl) diluted with deionised water to form concentrations of 1.5, 3.0, 6.0, 15, 150, 300 and 1500mg NH_4^+-N per litre, respectively, equivalent to 0.01, 0.02, 0.04, 0.1, 1.0, 2.0, and 10mg NH_4^+-N per gram of dry woodchip for every 200ml of solution. Samples were hand shaken to ensure a proper mix with the ammonium solution and were kept at 4^oC prior to analysis. Sampling was carried out at T0, T7, T14, T30, T45 and T60. For both adsorption and desorption experiments, the samples weight (volumes) before and after sampling (filtration) was obtained using the data from the WCH experiment, which contained the same mass of dry woodchip, added volume of deionised water and sampling intervals.

Adsorption. Samples were taken from the cold store and mechanically shaken for 30 minutes at 150 rpm. Subsequently, a volume of c.30ml from of each bottle was poured into a Whatman N^o2 paper filter by use of a perforated lid. The filtrates were then sent to the laboratory and analysed for NH_4^+-N by an automated segmented flow colorimeter on a Skalar auto-analyser. At T0, samples were left for 1 hour at room temperature before being mechanically shaken for 30 minutes at 150 rpm. Adsorption was expressed as a percentage of the difference between initial NH_4^+-N mass applied and final NH_4^+-N mass in extraction, in proportion to initial NH_4^+-N mass applied. It has been considered that a small proportion of the NH_4^+-N that would appear to be adsorbed corresponds to NH_4^+-N entrained within the particles.

Desorption. For desorption of NH_4^+-N, the remaining water in each bottle was discharged and 200ml of deionised water added. Samples were hand shaken and left for 1 hour at room temperature after which were mechanically shaken for 30 minutes at 150 rpm and c.30ml of each bottle was poured into a Whatman N^o2 paper filter by use of a perforated lid. Samples were then sent to the laboratory and analysed for NH_4^+-N by automated segmented flow colorimeter on a Skalar auto-analyser. Desorption was expressed as a percentage of the difference between NH_4^+-N mass desorbed by the woodchip and the remaining adsorbed NH_4^+-N mass (that which remained within the woodchip after the first adsorption extraction).

Statistical analysis. Data from the water holding capacity experiment for both sawdust and G30 were analysed using a linear-by-linear rational function o rectangular hyperbola, in Genstat. Data from the NH_4^+-N adsorption and desorption experiments had to be analysed with the use of different functions due to differences in performance of the two woodchip type. For G30 adsorption and desorption, an exponential function was fitted using Genstat. For sawdust no define pattern was found, and for this reason a linear function was fitted for both adsorption and desorption data, using a group regression and F test (Fisher), in Genstat.

Results and discussion

Physical properties of woodchip

The initial water content of sawdust was 38% (±0.9%) (expressed in proportion to its initial moist weight) and 180% (±7.5%) when expressed respect to its dry weight. For G30 these values were 43% (±0.2%) and 130% (±1.2%), respectively. Density of the woodchip was 294 (±9.2) and 360 (±7.6) kg m^{-3}, for sawdust and G30, respectively. No value was found in literature for density of timber for sawdust material due to its palleted origin. However, the woodchip density determined for G30 in this experiment was within the range found by Dalla-Salda et al (2009) for timber density values of Douglas fir (Pseudotsuga menziesii), between 350 to 500 kg m^{-3} (Table 1).

In relation to the characterisation of the woodchip particles, it was obtained that sawdust presented smaller particles sizes in proportion to its bulk volume, than G30. More than 50% of the bulk volume of sawdust is composed by particles smaller than 2.0mm.

Table 1. Chemical characteristics and composition of the woodchip material.

Woodchip type	TN[a]	NH_4^+-N[b]	NO_3^--N[d]	TP[c]	Total Carbon	C:N Ratio	D.M	MC[e]	WD[f]	PD	CEC[i]
	mg/100g dry weight basis						%	% DW	kg m^{-3}	kg m^{-3}	mmol/100g DM
G30	65	6.3	0.3	18	22620	348	43	130	360	350-500[g]	7.4
Sawdust	1440	69.8	0.5	13	33120	23	36	180	294	219-227[h]	14.3

(a) Total nitrogen (Kjeldahl); (b) Ammonium-nitrogen (Kjeldahl); (c) Total phosphorus; (d) Nitrate-nitrogen; (e) Moisture content; (f) Woodchip bulk density, fresh weight basis; (g) Particle density, Dalla-Salda et al (2009) and (h) sawdust bulk density by Ragland et al (1991); (i) Darch (2009).

For G30, the range of particle size of 2.0-1.0mm accounted for only 2.2% of its bulk volume and that particles in the range between 9.5 and 4.0mm represented nearly 50% of its bulk volume and 21% in sawdust. G30 also was composed by up to 27% of its bulk volume by particles between 20.0 and 9.5mm (Table 2). This considerable difference between particle sizes in sawdust and G30 may suggest a considerable variation in surface area. Sawdust is expected to have a larger surface area than G30.

Table 2. Particle size characterisation for sawdust and G30.

Sieve	Sawdust		G30	
mm	Bulk weight %	s.e.	Bulk weight %	s.e.
20.0 – 9.5	-	-	27.0	1.51
9.5 – 4.0	21.2	0.24	49.5	1.38
4.0 – 2.0	27.9	0.59	21.1	0.32
2.0 – 1.0	30.4	1.16	2.2	0.03
1.0 – 0.5	15.7	0.45	-	-
0.5 – 0.15	4.7	0.11	-	-

Water holding capacity

Water holding capacity measured after 62 days was found greater ($P<0.05$) on sawdust (366%) than G30 (230%). For T0, sawdust was found to hold within it matrix more than twice its dry weight in water (230%), while this value was lower for G30 (76%) (Table 3), meaning that these values are the starting point of minimum water holding capacity by both woodchip types. During the first week of submersion the WHC of sawdust and G30 increase at a mean rate of 14.4and 17.1% d^{-1}, respectively, which was faster than the rate observed during the following seven weeks (0.6% d^{-1} for both woodchip type). However, during the first hour of submersion sawdust and G30 had a 293 and 144% WHC, which is equivalent to 80.0 and 62.6% of their maximum WHC, respectively.

These results are supported by Airaksinen et al (2001) who found that sawdust was the most absorbing material amongst many others with a WHC of c.250% during the first hour of submersion. However, Molnar & Wright (2006) reported that pine shavings had a WHC of 90% at 1 hour submersion which is contrasting to the findings of Ward et al (2000) who found values of450% WHC for the same material and submersion time. In other studies on WHC of woodchip materials, Luo & Lindsey (2006) found that fine and coarse pine bark and the mixture of coarse bark and zeolite had no significant differences between them, with average WHC of 58, 56 and 51%, respectively.

Table 3. Water holding capacity of both woodchip types over a maximum submerged time of 62 days.

Time submerged		Sawdust		G30	
		WHC %	s.e.	WHC %	s.e.
0 (entrained)		231	7.522	76	3.219
0.5	Hours	275	8.023	138	10.458
1		293	8.110	144	3.528
3		301	6.788	151	3.819
6		306	6.930	155	3.884
24		316	11.591	165	3.219
3	Days	327	11.092	181	9.615
7		332	3.215	196	8.293
14		339	11.465	201	6.360
30		341	5.674	211	6.521
44		353	4.324	221	6.825
62		366	4.919	230	6.858

An exponential function was obtained for sawdust and G30 with fitted curves presented in Figure 2. An exponential function was also tested, but this type of function did not fit due to tendency towards a step function or an asymptotic regression, due to the difference between the rapid water holding performance obtained during the first week -which had an exponential curve, and the straight-line shape of the curve obtained from submersion day 7 onwards (Figure 2).

The shape of the exponential curves between sawdust and G30 was not significantly different ($P>0.05$), but the position on the Y axis was significant ($P<0.05$), meaning that the water holding performance was significantly different between sawdust and G30.

Studies on other materials also suggest a degree of variability in WHC. Goto & Yokoe (1996) for example, found that untreated straw had an overnight WHC of 73%; Molnar & Wright (2006) suggest values of 160% for wheat straw, while reports from Airaksinen et al (2001) indicate that straw reached as little as 15.6% WHC after an overnight submersion. The experimental straw, the submersion time and method may lead to contrasting results between authors. For example, Schofield (1988) reported that submerging barley straw for 2h and then draining it for two additional hours gave WHC values of 186 and 249% for chopped and whole straw, respectively. After a further draining period of 24h, the author reported that their WHC was 129 and 157%, respectively.

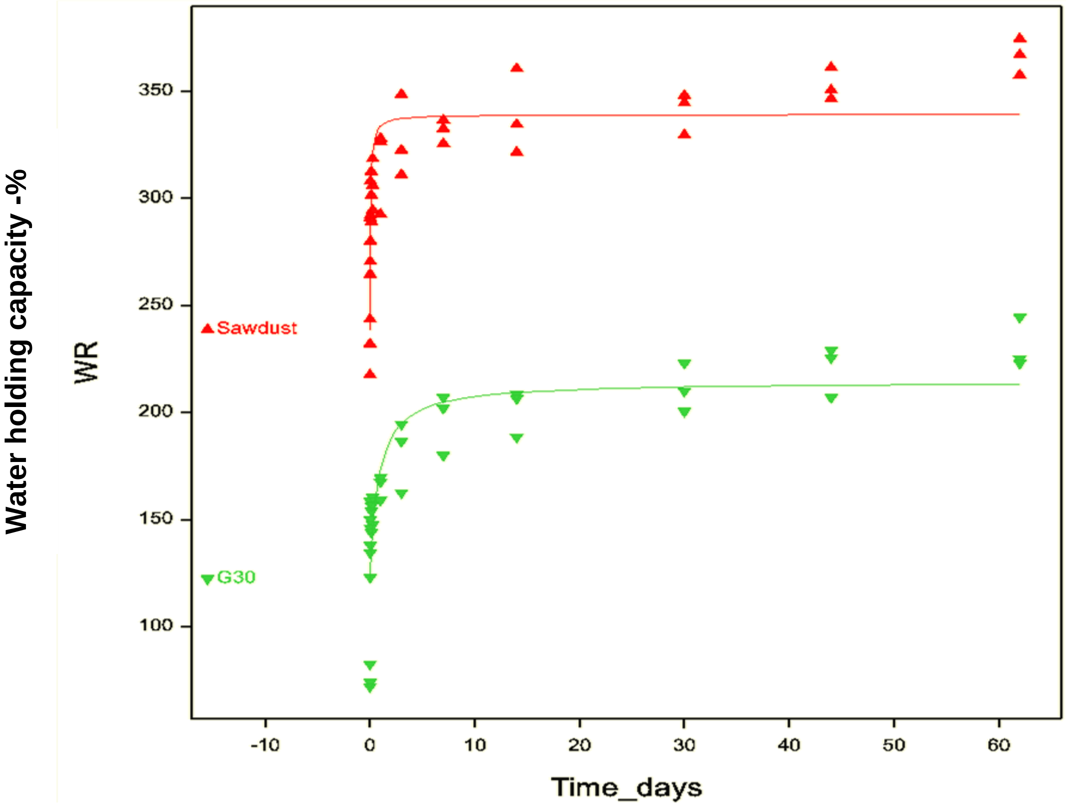

Figure 2. Water holding capacity of both woodchip types measured over a submersion period of 62 days. Both curves do not start at 0 due to the capacity of the woodchip to instantly entrain water within its matrix. This water was not considered as adsorbed.

On a similar study, it was found that chopped straw had lower water absorption than whole straw, with mean values of 248 and 269% WHC (Deininger et al., 2000). The author also found that after draining both straw materials for a centrifuging period of c.9min, the WHC was reduced to 73 and 81%, respectively.

To reduce bedding compaction cattle is feed outside the pads, to avoid an accumulation of dung and solids in the same area of the pad, and therefore to avoid an intense flux of cattle excreta on one place, having direct implications of the effluent quality. Additionally, by feeding cattle outside the bedding area, it insures an even distribution of dung and urine within the whole of the woodchip area and therefore securing that the effluent concentration is kept constantly low throughout its use.

As previously discussed, the WHC of both woodchip materials increased abruptly (power curve distribution) during the first 7 days and then continued gradually until day 62. However, the capacity of both woodchip materials to retain water did not reach a saturation point during the experimental period, suggesting that both sawdust and G30 had still the capacity to hold more water than that observed.

Ammonium-N adsorption and desorption capacity of both woodchip materials: sawdust and G30

The samples sent for analysis containing both adsorption and desorption extractions from the higher concentrations used in this experiment as submersion solutions (150, 300 and 1500 mg l^{-1}) encountered an error during analysis due to internal calibration ranges by the Skalar auto-analyser.

Because this error gave fault values for both wood-residue types and sampling intervals, results from the lower concentrations (1.5, 3.0, 6.0 and 15 mg l^{-1}) are presented only.

Sawdust. Ammonium-N adsorption and desorption capacity

A linear function was fitted for both adsorption and desorption data due to the lack of a define pattern of the fitted values. Significant differences ($P<0.05$) were found between the treatments' response to the four concentrations. A positive adsorption correlation with time was only observed for the treatment of 15 mg l^{-1}. The lowest (-1257%) and highest (80.9%) NH_4^+-N adsorbency rates by sawdust were obtained in the 1.5 and 15 mg l^{-1} solution, respectively, after 60 days of submersion (Fig.3a). The same treatment of 15 mg l^{-1} also resulted in the lowest desorption rate after 60 days, suggesting that high NH_4^+-N adsorption may imply low NH_4^+-N desorption (Fig. 3b).

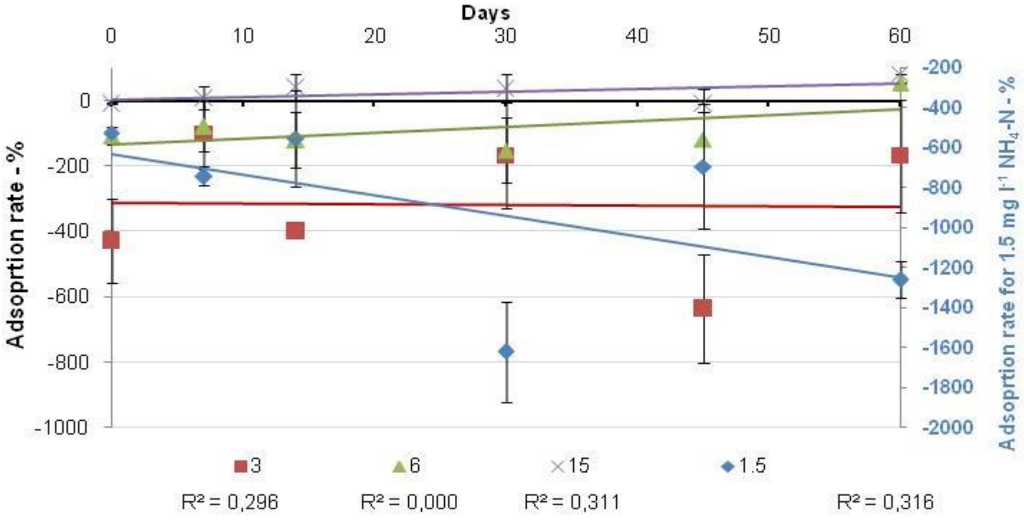

Figure 3a. Sawdust ammonium-N adsorption rate. The treatment at 1.5mg l^{-1} concentration was plotted in secondary axis to facilitate the observation and performance of the other three treatments.

The high content of NH_4^+-N in the sawdust particles may suggest a key aspect behind the negative and extreme adsorption values, especially when submerging the woodchip material to low NH_4^+-N concentrations, as seen for the 1.5 mg l^{-1} of NH_4^+-N which recorded this extreme response (Fig 3a). Due to the high concentration of NH_4^+-N in sawdust, adsorption results gave negative values, indicating that rather than adsorbing NH_4^+-N the particles release this constituent making the concentration in the solution increase (Fig 3b).

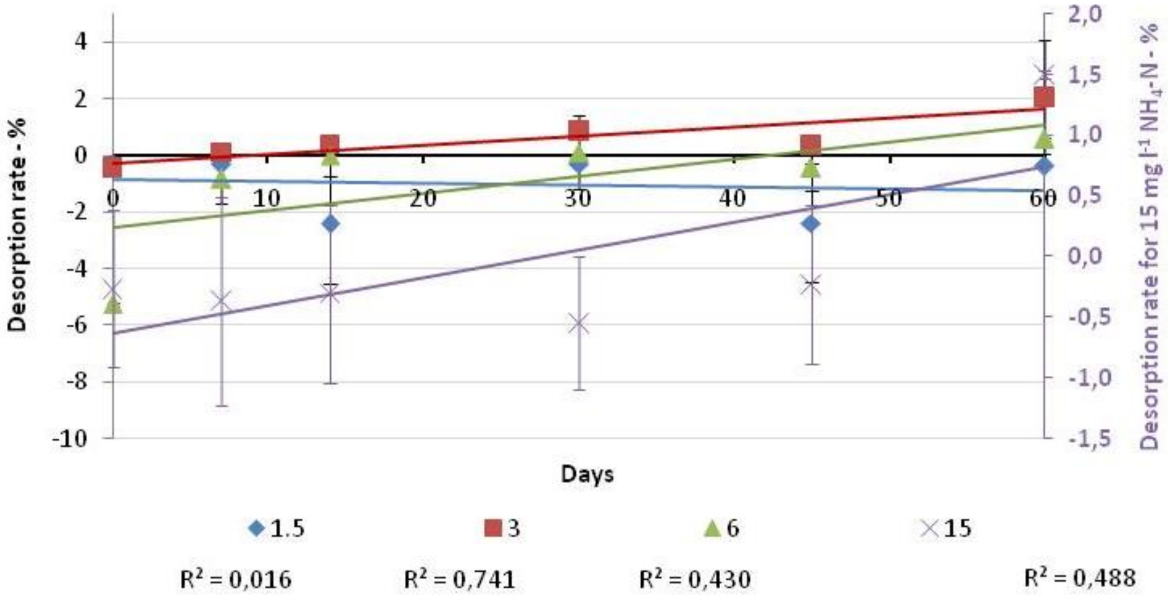

Figure 3b. Sawdust ammonium-N desorption rate. The treatment at 15mg l^{-1} was plotted in secondary axis to facilitate the observation and performance of the other three treatments.

A crucial aspect of the NH4+-N adsorption and desorption capacity by woodchip is determined by their capacity to hold water, because this will define how well they adsorb the NH_4^+-N found dissolved in the liquid fraction of the deposited slurries. However, although sawdust had a significantly higher ($P<0.05$) WHC than G30, it showed lower capacity to adsorb NH_4^+-N.

G30. Ammonium-N adsorption and desorption capacity

This woodchip material presented a clear relationship between adsorption rate and time submerged, compared to sawdust. A good correlation between time submerged and adsorption rates was obtained (Figures 4 and 5). An exponential function was fitted for adsorption and desorption. As NH_4^+-N concentration in submerged solution increased, so did the amount of NH_4^+-N adsorbed, as well as the adsorption rate increasing with time, suggesting that important surface binding processes occur with time and concentration (Fig 4).

All treatments reached a maximum NH_4^+-N adsorbency capacity of 79.2, 88.6, 84.2 and 82.4% for 1.5, 3.0, 6.0 and 15 mg l^{-1} treatments, respectively. On average, during the first 14 days of submersion, all treatments had adsorbed c.72.5% (± 1.47) of the NH_4^+-N, and approximately a further 11% during the following 45 days (Figures 4 and 5).

The amount of NH_4^+-N adsorbed by G30, increased with increasing NH_4^+-N concentration in the submerged solution, but with no numerical differences between submersion times. When comparing submersion time with adsorption rate, it was found that sawdust had the highest adsorption rate when submerged in the highest NH_4^+-N solution (c.90% adsorption), and the rate was constant throughout the 60 days (Figures 4 and 5).

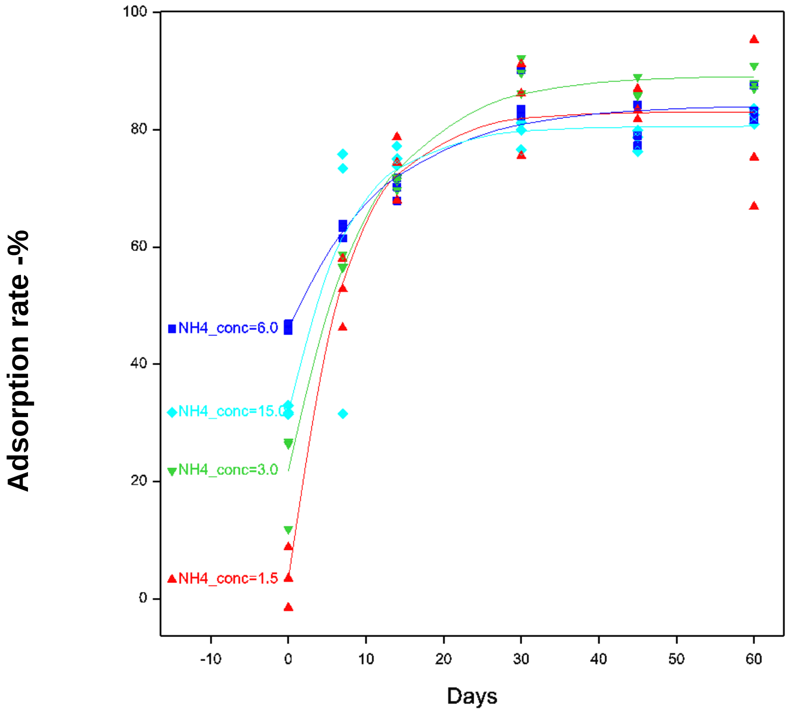

Figure 4. G30 ammonium-N adsorption capacity. Adsorption rate/submersion time.

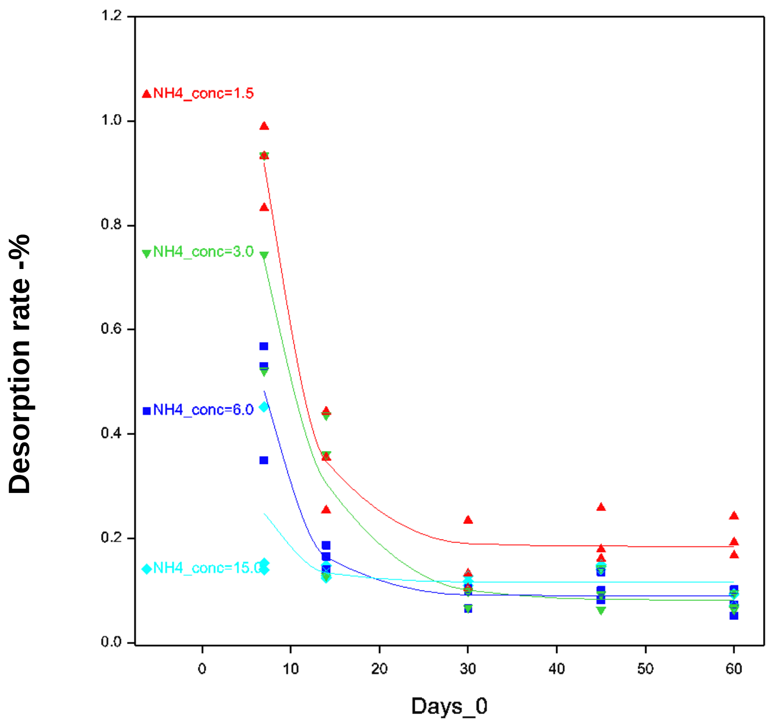

Figure 5. G30 ammonium-N desorption capacity. sorption rate/submersion time. Desorption rates at T0 for all concentrations were not included in the graph due to extremity with values that made the observation of the plotted data not clear.

Overall discussion

The chemistry of NH_4^+ and NH_3 on how it dissociates and links to other molecules such as hydroxide ions (OH^-), and chloride (Cl^-) when present in aqueous solutions (H_20) has been a complex matter (Cotton & Wilkinson, 1972).

Due to the weak acid nature of the ammonium ion (NH_4^+), when added into aqueous solution as ammonium chloride (NH_4Cl) it easily dissociates into three components: aqueous ammonia (NH_3(aq)), aqueous hydronium cation (H_3O^+(aq)) and a free atom of chloride (Cl^{-1}) making the solution slightly acidic(Kaurav, 2011). Cotton & Wilkinson(1972) state that due to the extreme solubility of ammonia in water, when present in aqueous solutions it links to water (H_2O) molecules by hydrogen bonds, remaining hydrated and not in a gaseous form.

On the basis that the addition of NH_4Cl to water turns the solution slightly acidic, it can be expected that changes in pH are likely to occur. If the pH of the solution is affected then variations in the CEC of woodchip are possible, which in turn could have an impact on the NH_4^+-N adsorbency rate by the woodchip material. It has been reported that an increase in pH from 3.5 to 11.5 can reduce adsorption rate of metal complex dyes by pine sawdust from 65% to 15%, respectively (Ozacar & Sengil, 2005), as also supported by Shukla et al (2002).

Differences in the CEC of any adsorbent material have shown to have an impact on the capacity of the material to adsorb and desorb positively charged ions. Lee (2011) reports CEC values in red pine wood (Pinus resinosa Ait.) of 9 mmol/100g at pH 7, and that the CEC reached 20 mmol/100g when pH was increased to 11. Similar results were reported by Kamdem & Zhang (2000, in Lee, 2011) were at pH 7 pine wood had a CEC of 9.1 mmol/100g. These results are within the range of the CEC values used in this experiment which are based on reports from Darch (2009) who found that the CEC of sawdust and G30 were 14.3 and 7.4 mmol/100g, respectively. The difference in CEC between sawdust and G30 correlates to the higher WHC and ammonium adsorption rate found in sawdust, and the lower WHC and adsorption rate in G30. It also correlates to their low NH_4^+-N desorption rates, which were slower in sawdust due to its high CEC. However, these CEC are quite low compared to reports on other materials. CEC in soils is in the range of 0 and 50 mmol/100g for sand and clay, respectively (Yara Analytical Services, 2012), as also reported by who found values for sandy soils to be in the range of 0.5 to 5 mmol/100g and up to 50 mmol/100g for clay soils (Camberato, 2001), while the same author reports CEC values for zeolite between 1-200 mmol/100g.

On the basis that the high ammonium chloride solution concentrations of 15 mg l^{-1} makes the solution slightly more acidic, then this would suggest a decrease in solution pH which could decrease CEC of the woodchip material thereby decreasing the water holding and NH4-N adsorbency capacity. However, the concentrations used in this experimental study were in the range of 6-57 mg l^{-1} (compared to the c.1500 mg l^{-1} of NH_4^+-N in cattle slurry), so little changes in pH can be expected to occur and therefore low impact on CEC changes that would have increased surface binding sites and thus NH_4^+-N adsorption. A report has shown that a 5.0% w/v aqueous solution (50000 mg l^{-1}) of ammonium chloride has a pH in the range of 4.6 to 6.0 (Bothara, 2007).

Differences in surface area of the woodchip materials could similarly impact the adsorption and desorption rates of NH_4^+-N. On the basis of the difference obtained in the characterisation of particle sizes between sawdust and G30, where sawdust was composed by very fine particles, it can be expected that sawdust would have a greater surface area suggesting that this material would record higher levels of adsorption than G30. A report show that a decrease in particle size increases surface area and adsorption opportunity at the outer surface of woodchip materials (Shukla et al., 2002). However, sawdust having a larger surface area had a lower capacity to adsorb NH_4^+-N than G30 which had bigger particle sizes and therefore a smaller surface area and greater capacity to adsorb NH_4^+-N. This notes that a more predominant process controls adsorption and desorption of NH_4^+-N in the woodchip materials used in this experimental study.

What appears to be another important process associated with adsorption and desorption of NH_4^+-N from woodchip is changes in osmotic pressure. Several studies have shown that the addition of ammonium chloride to aqueous solutions increases osmotic pressure (Sayed & Kenny, 1978; Darrah et al., 1986; Darrah et al., 1987).A greater capacity to adsorb NH_4^+-N was observed by G30 which had lower CEC than sawdust which, on the other hand, reported a lower capacity to adsorb NH_4^+-N.

On the basis of this discussion so far it would be expected that adding a solution containing ammonium chloride to a low NH_4^+-N adsorbent material would create a contrast in osmotic concentration with the low NH_4^+-N pressure inside the material and the high NH_4^+-N pressure in the solution. This would therefore force the NH_4^+-N from high pressure to move into the material until both the solution and the woodchip reach a point of equilibrium. However, few studies were found on how osmotic pressure can affect NH4-N adsorption (Abdoun et al., 2003).

However, the solutions prepared in this experiment had a NH_4^+-N concentration of 0.01, 0.02, 0.04 and 0.1 mg g^{-1} of dry woodchip (1.5, 3.0, 6.0 and 15 mg l^{-1}), whereas the NH_4^+-N content of the woodchip materials were 0.69 and 0.063 mg g^{-1} dry woodchip, for sawdust and G30, respectively. This will suggest that because sawdust contains sevenfold NH_4^+-N per gram of material (0.69) than the concentration of the submerged solution (0.01-0.1) the high pressure will be found inside the woodchip rather than in the solution, forcing the NH_4^+-N to move towards the aqueous solution. This can clarify why the lower NH_4^+-N solutions have negative adsorption and why the highest NH_4^+-N solution treatment gave positive adsorption rates.

The G30 woodchip material, contained tenfold less NH_4^+-N (0.063 mg g^{-1} dry woodchip) than sawdust, and an NH_4^+-N within the range of concentration of the submerged solutions and even lower than the 15 mg NH_4^+-N l^{-1} treatment. This implies that a high osmotic pressure is more likely to impact adsorbency rate than sawdust, and the results in this experimental study widely support this.

Based on the possible changes in osmotic pressure it can be expected that the treatments that were able of reaching the highest NH_4^+-N adsorbency should, on the contrary, present the lowest capacity to desorb the NH_4^+-N adsorbed. In fact, for G30 -which had good adsorption/desorption curves and correlations- (see Figure.4), the order from highest to lowest adsorbency at 60 days was 3.0, 6.0, 15 and 1.5 mg l^{-1}, and the reverse order was found for highest to lowest desorbency at 60 days; 1.5, 15, 6.0 and 3.0 mg l^{-1} of NH_4^+-N. The same effect occurred in sawdust, were the treatment of 15 mg l^{-1} which recorded the highest adsorbency of NH_4^+-N was also the treatment with the lowest desorption rate. This correlates as previously discussed that submerging woodchip to high concentrations of NH_4^+-N creates a strong intra-particle bond than when submerged to a lower NH_4^+-N concentration.

Although WHC was greater in sawdust, this woodchip material did not reach greater adsorption rates as G30 (which in turn had lower WHC). This may suggest that WHC is not a primary role player in determining the properties of NH_4^+-N adsorption by woodchip. However, it was observed that NH_4^+-N adsorption by G30 occurred more rapidly during the first 14 days of experiment, period in which water adsorption by this woodchip material was exponentially fast.

Wood residues (G30) showed great capacity to adsorb NH_4^+-N to levels up to nearly 90% whilst demonstrating low desorption capacity of NH_4^+-N (less than 1%). These are ideal relevant features as an adsorbent material for the removal of nutrients (or heavy metals) from contaminated waters such us farm o industrial effluents, or even for the depuration of eutrophic watercourses. This could help reduce the concentration of farm effluents making them more manageable, subsequently contributing towards the compliance of new environmental regulations.

Despite the differences in CEC between wood residues, no correlation was found with this parameter and adsorption or desorption. Expected changes in pH appeared not to be sufficiently important to cause changes in CEC.

Osmotic pressure appears to be a more predominant parameter controlling processes of adsorption and desorption of NH_4^+-N in both wood residues, above surface area and CEC.

Wood residues high in NH_4^+-N should be avoided, as they can have an opposite effect in the adsorption of nutrients from nutrient-rich effluents, leading to the release of nutrients from the wood residue to the environment.

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