SHORT COMMUNICATION

ADSORPTION OF ATRAZINE AND HEXAZINONE IN A SUGARCANE SOIL AMENDED WITH COAL FLYASH

SOOBADAR A AND NG KEE KWONG R

Mauritius Sugar Industry Research Institute, Réduit, Mauritius
amooniaruck@msiri.intnet.mu RNKKwong@msiri.intnet.mu

Abstract

The sugar cane industry in Mauritius uses 400 000 tonnes of coal for cogeneration during the intercrop season to optimize the viability of the enterprise. In so doing, 20 000 t/annum of coal ash are produced and have to be judiciously disposed of, with minimal risk to the environment. Agricultural recycling of these wastes is deemed to be the most sensible option for its disposal. However, when 100 t/ha of coal flyash were applied to sugarcane soil, a higher proliferation of weeds was observed than when only NPK fertilizers were used. This therefore suggests that herbicides were being effectively adsorbed by the flyash, thereby reducing significantly their potency in soil. For this reason, the adsorption of atrazine and hexazinone (concentration of solutions equivalent to their recommended rates), on a mixture of soil and coal flyash added to reflect application rates of 100 t/ha was studied using batch equilibrium. The results showed that coal flyash, because of its higher surface area, adsorbed more herbicides than the soil. It also had a higher affinity for atrazine and hexazinone with sorption coefficients (K_L) of 3.13 for atrazine and 7.69 for hexazinone as opposed to 0.09 for atrazine and 0.13 for hexazinone, with soil only. These results imply that coal flyash reduces the transfer of herbicides to groundwater; however, to control weeds more frequent applications or three times the recommended dose of hexazinone (1.2 kg a.i/ha) and 10 times the recommended dose of atrazine (2.4 ka a.i/ha) will have to be used.

Keywords: herbicide, sorption, weed control, waste recycling, crop production, isotherm

Introduction

Through the combustion of 440 000 tonnes of coal during the intercrop season for cogeneration purposes, the sugarcane industry in Mauritius generates around 20 000 tonnes of coal flyash which has to be disposed of judiciously. Agricultural reuse of the flyash has been deemed the most sensible option for its disposal. However when coal flyash was applied at 100 t/ha prior to planting of sugarcane in Mauritius, a higher weed proliferation occurred than in fields receiving only mineral NPK fertilizers. The coal flyash had somehow diminished the potency of the applied herbicides in the soil. Gupta *et al.* (2002) had previously reported that flyash can indeed effectively adsorb herbicides, making them less bioavailable for controlling weeds.

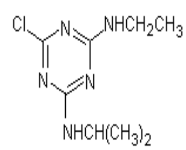
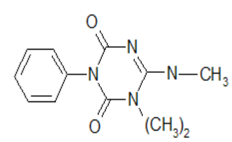
To ascertain whether coal flyash really enhances herbicide adsorption in soils, batch equilibrium studies were conducted in the laboratory on two herbicides commonly used in sugarcane cultivation in Mauritius, namely atrazine and hexazinone, using as adsorbent a soil amended with coal flyash at a rate equivalent to 100 t/ha.

Materials and Methods

Characteristics of the soil, coal flyash and herbicides used

The soil in the present study is an Oxic Humitropept receiving 1500 mm rain annually. The coal flyash was collected from the Belle Vue Thermal Power Station in Mauritius and was derived from bituminous coal. The chemical characteristics of the soil and coal flyash are shown in Table 1. Also shown are some major physicochemical properties of the herbicides atrazine and hexazinone (active ingredients with a purity of 96%).

Table 1. Selected chemical characteristics of the soil, coal flyash and herbicides atrazine and hexazinone used in this study.

Parameters	**Oxic Humitropept**	**Coal flyash**
pH	5.3	10.3
Organic Carbon (g/kg)	21.7	32.9
Cation Exchange Capacity	20.4	30.5
Particle size distribution		
% sand	9.2	nd
% silt	15.9	nd
% clay	75.0	nd
Silicon (g/kg)	0.65	5.78
Iron (g/kg)	134.5	20.8
Properties	**Atrazine**	**Hexazinone**
Structural formula		
Chemical formula	$C_8H_{14}ClN_5$	$C_{12}H_{20}N_4O_2$
Molecular weight	215.7	252.3
Water solubility (mg/L)	30	29 800
Dissipation half life (days)	10-12	17-29
Octanol water coefficient (K_{ow})	398	15
pKa	1.7	2.2

nd = not determined

Adsorption isotherms

To a mixture of 1.0 g soil and 0.4 g coal flyash, 1.0 g soil only and 0.4 g coal flyash in glass centrifuge tubes, 6.0 ml distilled water spiked to contain initial concentrations of atrazine of 2.40, 4.77 and 9.39 µg/ml and hexazinone of 0.89, 1.77 and 3.48 µg/ml respectively, were added, with each spiking concentration replicated twice. The lowest spiking concentration of each herbicide solution was equivalent to the field recommended rates of 1.2 kg a.i./ha for hexazinone and 2.4 kg a.i./ha for atrazine. The ratio of soil to coal flyash used was chosen to reflect an application rate of 100 t/ha of coal flyash to the soil.

Control tubes containing only atrazine and hexazinone solutions but no sorbent were included to quantify losses due to volatilization or sorption to the tube components. The soil and the soil/coal flyash mixture were also equilibrated with distilled water which had not been spiked with the herbicides, to ensure that no desorption of atrazine or hexazinone was occurring from the soil. All tubes were continuously shaken in the dark at 4°C for 17 and 240 hours respectively; these two equilibration times were chosen because the objective of this study was to verify what was happening under field conditions. After 17 and 240 h, 1.0 ml of the liquid phase was withdrawn with a syringe, centrifuged for 10 mins, decanted and mixed with acetonitrile to produce an extract of 1:4 water : acetonitrile, before being injected directly into the HPLC equipped with a diode array detector for the determination of atrazine and hexazinone concentrations.

The experiment results were fitted to the Langmuir isotherm model which can be written as follows:

$$C_s = \frac{C_{smax} K_L C_e}{1 + K_L C_e}$$

where

C_s = is the amount of herbicide adsorbed as a monolayer per unit of adsorbent at equilibrium

C_{smax} = is the maximum amount of monolayer herbicide adsorbed at plateau per unit of adsorbent

C_e = is the concentration of herbicide in aqueous phase at equilibrium

K_L = is the coefficient of Langmuir, relating the affinity of the adsorbate to the adsorbent.

Results and discussion

Adsorption isotherms

Figure 1 shows the adsorption isotherms of atrazine and hexazinone at 4°C onto the various adsorbents studied. Adsorption of the two herbicides was enhanced after both 17 and 240 h equilibration when the soil was amended with the coal flyash.

The higher adsorption of the herbicides by coal flyash when compared to soil may be attributed to the higher surface area exposed to the ash. Indeed, mineralogical studies have shown that 70-90% of coal flyash particles are minute glassy spheres ranging from 0.01 to 100 µm in size (Adriano *et al.,* 1980). Coal flyash has in addition a significant residual carbon content which enhances adsorption, as reported by Banerjee *et al.* (1995).

Fitting the adsorption data of atrazine and hexazinone to the Langmuir equation to obtain values of C_{smax} and K_L gave high r^2 (>0.72), indicating that the Langmuir isotherm model fitted the experiment data well. The maximum adsorption capacity (C_{smax}) of the herbicides with coal flyash was found to be 39.6 µg/g for hexazinone and 212.0 µg/g for atrazine, while for the mixture of soil/coal flyash it was reduced to 26.3 µg/g for hexazinone and 76.8 µg/g for atrazine. As expected, values were higher than those found for the soil only, namely 12.4 µg/g for hexazinone and 53.2 µg/g for atrazine after 17 h of equilibration time. Calculations of K_L, which reflect the affinity of the adsorbent for the herbicide, gave K_L values of 7.7 for hexazinone and 3.1 for atrazine for coal flyash as compared to 0.1 for hexazinone and 0.1 for atrazine for soil only. This confirmed that coal flyash was more effective than soil in adsorbing atrazine and hexazinone.

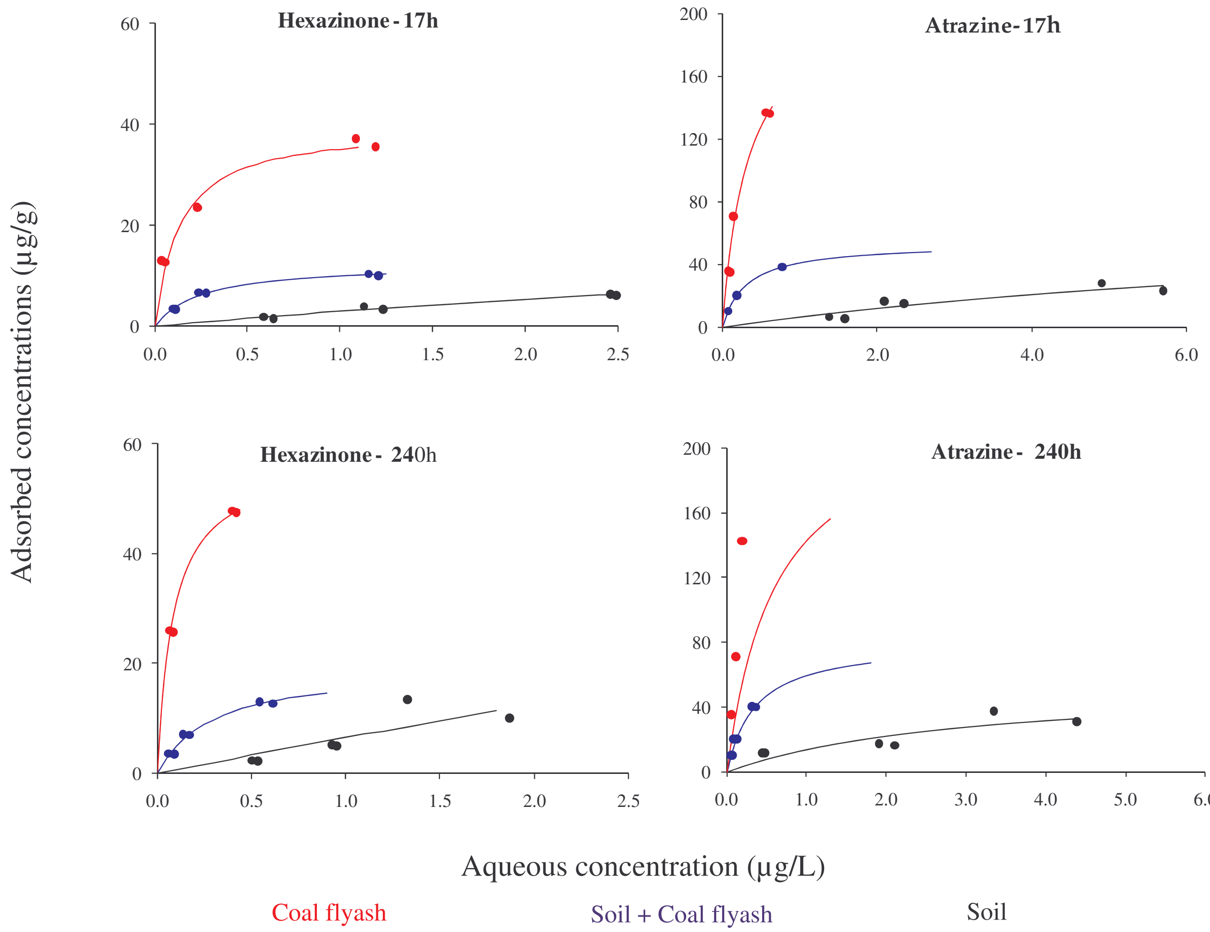


Figure 1. Langmuir isotherms for adsorption of atrazine and hexazinone at two different equilibrium times (17 and 240 h). The points correspond to experiment results and the lines are derived by feeding experiment points in the Langmuir Equation using software Win Reg 3.3 (Debord, 2007).

Conclusions

The present study showed that coal flyash, due to its greater affinity and higher surface area, adsorbed more hexazinone and atrazine than soil alone. The adsorption is adequately described by Langmuir isotherms. Studies (e.g Iglesias *et al.*, 2009), have shown that soil applied herbicides reach surface and groundwater by runoff and leaching. This study demonstrated that reduction in herbicide movement in soils may be achieved by adding coal flyash. If, from the environmental point of view, this increased immobilisation of herbicides is most desirable; from the agronomic point of view effective control of weeds would imply more frequent or higher application rates of hexazinone and atrazine. This would in turn increase environmental risk and costs of application. Based on comparison of the aqueous concentrations of atrazine and hexazinone in soil and in the soil/coal flyash mixture after 17 and 240 h of equilibration time, the rate of hexazinone must be raised to three times the recommended rate of 1.2 kg a.i/ha and that of atrazine 10 times the recommended rate of 2.4 kg a.i/ha. In addition, adsorption should not be regarded as permanent, and under certain conditions desorption can occur. High rates of coal flyash should therefore not be disposed on sugarcane lands, particularly as it has already been demonstrated that doing so would lead to a reduction in sugarcane productivity even when weeds are effectively controlled (Soobadar *et al.,* 2010).

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