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Sugarcane trash ash: A low cost adsorbent for atrazine and fipronil removal from water

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The sugarcane trash ash (STA) has been explored as low cost adsorbent for atrazine and fipronil removal from water. Kinetics study suggested that the pseudo second order model best explain the adsorption of both pesticides. The STA show higher adsorption of fipronil (K_d - 1267.5-3321.1) than atrazine (K_d - 137.0-1445.3) while desorption followed reverse trend with 0-2.27 and 4.83-9.32% fipronil and atrazine desorption, respectively. Isotherm model optimization suggested that the Freundlich isotherm best predict the adsorption-desoprtion behaviour of pesticides. Adsorption is highly nonlinear as 1/n values were 0.23 and 0.407 for atrazine and fipronil respectively. Adsorption decreased with increase in initial concentration of pesticide in solution. The sugarcane trash, a waste, can be used as energy source in boilers and the ash obtained can be utilized as low-cost adsorbent for pesticide removal from contaminated water.

Keywords: Biomass ash, Pesticide removal, Modelling, Kinetics, Adsorption

The sugarcane trash (or cane trash) is leaves that are left over in the field after the sugarcane is harvested. Farmers usually burn the trash since it is resists biodegradation, highly indigestible as fodder, has a low density biomass and is bulky to transport. Sugarcane is the third important crop after rice and wheat whose residues are burnt on field in India and Uttar Pradesh contribute maximum to the burning of sugarcane trash followed by Karnataka[1]. However, cane trash is an excellent biomass resource in sugar-producing countries worldwide, which is wasted for easy crop harvest and land clearing. The amount of cane trash produced depends on the sugarcane variety and age of the crop at harvest and generally, it represents about 15% of the total above ground biomass at harvest (about 10-15 tons per hectare of dry matter). The plant biomass can be used to generate energy and cane trash has high calorific value as it is dry in nature. Its use in boilers can save huge energy bill.

Reports on pesticide contamination of groundwater and surface water have gained serious attention from the public health safety point of view. Atrazine, a triazine group of herbicide is in the hit list[2,3]. The EPA[4] has classified atrazine as class C chemical ("possible human carcinogen") and has the maximum contaminant level (MCL) in drinking water 3.0 mg L^{-1} and below 0.1 mg L^{-1} for the European Union. Fipronil is the most commonly detected insecticide in the water samples collected from Sacramento, San Francisco Bay and Orange County and residues were above their lowest USEPA aquatic benchmark[5,6]. Activated carbon based adsorption is the most commonly used process for the removal of contaminant from wastewaters; however, high cost of adsorbent limits its use[7-9]. Search for new, cheap and indigenously available materials for pesticide removal from water and waste water have been the focus of recent studies.

Plant biomass ashes, which contain significant amount of unburnt carbon, have shown considerable capacity to adsorb pesticides from water[10-14]. Ashes generated from the sugarcane bagasse, mustard plant, rice husk and rice and wheat straw have been evaluated for removal of 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDT), 2,2-bis(4-chlorophenyl)-1,1-dichloroethene (DDE), lindane, malathion, 2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxyacetic acid (MCPA), diuron and pretilachlor from water[15-21]. Effect of *p*H, adsorbent dose, particle size and temperature on removal efficiency of pesticide was evaluated and results suggested that high surface area and porosity of unburnt carbon in ashes was responsible for pesticide adsorption. Kinetics studies suggested that pseudo-second-order (PSO) kinetic model best explained 2,4-D adsorption on mustard plant ash and suggested that the was the best fitted kinetic model. Deokar *et al*[18]. reported that the rice husk ash was ~2.3 times (weight basis) and ~55.55 times (surface area basis) better than the activated carbon in adsorbing MCPA. However, ashes differ in their physico-chemical properties and ability to retain pesticides depending upon the nature of the biomass used. Absolutely no information is available on the use of the sugarcane trash ash (STA) for removal of pesticides from water. Therefore, present study reports the atrazine and fipronil adsorption kinetics and isotherm modelling on to the STA as low cost adsorbent.

Experimental Section

Chemicals

Analytical grade atrazine (purity - 98.9%, P_{ow} - 2.82, water solubility - 33 mg L^{-1} at pH 7) and fipronil (purity – 97.5%, P_{ow} – 4.0, water solubility – 1.9 mg L^{-1} at pH 7) was purchased from the Sigma-Aldrich, India. Solvents used were purchased locally and were of analytical grade.

Adsorbent

The sugarcane trash ash (STA) was used as an adsorbent. The sugarcane trash was dried in sun for two days and was burnt on field. Burnt residue (ash) was collected, ground, sieved and 60 BSS (British Standards Society) fraction was used. The samples were stored in air-tight PTFE containers at room temperature characterized for pH, organic carbon (OC) content, specific surface area (SSA) and porosity. Specific surface area and pore volume were estimated using the Brunauer, Emmett, and Teller (BET) nitrogen adsorption technique at 77K, using an automated manometric gas adsorption apparatus (Quantachrome NOVA 10.01, Quantachrome Instruments, Florida, USA). The properties of the STA were: pH - 10.5, OC – 8.21%, surface area – 27.23 $m^2 g^{-1}$, porosity - 0.0596 $cm^3 g^{-1}$.

Kinetics studies

The kinetics of pesticides adsorption on the STA was studied using batch method. The STA (10 mg for fipronil and 40 mg for atrazine, oven dry basis) and aqueous solution (20 mL of ~1 mg L^{-1} fipronil and 10 mL of 5 mg L^{-1} atrazine) of the pesticide in PTFE lined screw caped glass centrifuge tubes (30 mL) were equilibrated on a horizontal shaker. Two controls (without STA to know stability or sorption of pesticide on glass surface and without pesticide to know any interference during analysis) were maintained as controls and each treatment had three replicates. The samples were equilibrated for different time period *viz*., 0.5, 1, 2, 4, 6, 8, 12, 24 and 48 hr. After equilibration, the suspension was centrifuged using Sigma 3-16 KL centrifuge at 3139*g* for 20 min. The pesticides were quantified in the supernatant using high performance liquid chromatography (HPLC). The amount of pesticides adsorbed by the STA was calculated from the difference of initial and final concentration of the pesticide in the supernatant. During the equilibration period pesticides were stable as no decrease in their concentration was observed in the no ash control.

Adsorption studies

Adsorption of pesticides on the STA was studied using batch method at ash-water (w/v) ratios mentioned in the previous section. The concentration of atrazine ranged from 5 - 25 µg mL^{-1} for atrazine and 0.5 – 1.5 µg mL^{-1} for fipronil and each concentration was replicated thrice. Blanks, without ash, were maintained as control. The suspensions were equilibrated for 24 h and the amount of pesticide adsorbed was calculated as mentioned above.

Analysis

Aqueous samples were analyzed for the pesticides by directly injecting filtered samples (0.45 µm) in the HPLC (Varian, Prostar) equipped with quaternary pump, UV detector and Rheodyne injection system using Lichrospher C-18 stainless steel column [250 mm × 4 mm (i.d.)]. The conditions for atrazine analysis included: acetonitrile:0.1% aqueous *o*-phosphoric acid (70:30) at 1 mL min^{-1} flow and wave length of 222 nm. The conditions for fipronil were: acetonitrile:0.1% aqueous *o*-phosphoric acid (80:20) at 1 mL min^{-1} flow and wave length of 222 nm. Under these conditions the retention time for atrazine and fipronil was 3.7 and 3.8 min, respectively. The recovery of atrazine from water at 0.1, 1 and 10 µg mL^{-1} fortification levels was 92.8, 93.1 and 97.4%, respectively. The limit of detection (LOD) of method used was 0.01 µg mL^{-1} while the corresponding limit of quantification (LOQ) was 0.05 µg mL^{-1}. The recovery of fipronil from water at 0.1 - 1 µg mL^{-1} levels was >91.5%. The LOD and LOQ were 0.01 was 0.03 µg mL^{-1}, respectively.

Temporal adsorption kinetics models

Adsorption kinetics of pesticides onto the STA was studied using the linear form of the Lagregen pseudo-first order (PFO), pseudo-second order (PSO), Elovich and the intra-particle diffusion models.

Pseudo first order (PFO) $\text{Log}\ \{q_e - q_t\} = \log q_e - \{K_1/2.303\}t$ ... (1)

Pseudo second order (PSO) $t/q_t = 1/K_2 q_e^2 + \{1/q_e\}t$ ... (2)

Elovich equation $q_t = 1/\beta\ \text{In}\ (\acute{\alpha}\beta) + 1/\beta\ \text{In}_t$ ... (3)

Intra — particle diffusion model $q_t = [K_{int} \times t \exp (1/2)\ ] + C$ ... (4)

where, q_e is the amount of pesticide adsorbed at equilibrium (mg kg^{-1}), q_t is the amount of pesticide adsorbed (mg kg^{-1}) at time t (min), k_1 is the pseudo-first order rate constant (min^{-1}), k_2 is the rate constant of pseudo second order adsorption (kg $(mg\ min)^{-1}$), α_E is the initial sorption rate (mg kg^{-1} min^{-1}) and β_E is the desorption constant (kg mg^{-1}) during experiment. The intraparticle diffusion constant, k_i [mg $(kg\ min^{0.5})^{-1}$] was calculated by linearization of Eq. (4) as $q_t = k_i t^{0.5} + C$.

Adsorption isotherms models

Three commonly used 2-parameter adsorption isotherms *viz.*, the Freundlich isotherm, the Langmuir isotherm and the Temkin isotherm were used to model the observed data to know the best isotherm for explaining adsorption of atrazine and fipronil on to the STA.

Freundlich isotherm

$$\text{Log qe} = \text{LogK}_F + 1/n\ \text{LogCe} \quad \dots (5)$$

Langmuir isotherm

$$1/qe = 1/Q_0 + 1/Q_0 b_L C_e \quad \dots (6)$$

Temkin isotherm

$$C_S = \text{BlnA}_{Tem} + \text{BlnC}_e \quad \dots (7)$$

where, C_e is the concentration of pesticide in solution at equilibrium (mg L^{-1}) and K_F and 1/n are the Freundlich constants. The b_L (L mg^{-1}) is Langmuir adsorption constant while Q_o (mg g^{-1}) is the maximum monolayer coverage capacity. The A_{Tem} (L g^{-1}) is Temkin isotherm equilibrium binding constant, B is constant related to heat of adsorption (J mol^{-1}).

Results and Discussion

Kinetics studies

The results of kinetics of atrazine and fipronil adsorption onto the sugarcane trash ash (STA) clearly indicated that sorption of both pesticides increased with increase in the contact time, but rate of adsorption varied (Fig. 1). The sorption of fipronil proceeded fairly slowly and during first 0.5 h it was 14.14% while it was relatively fast for atrazine where 38.26% sorption was observed. This could be due to fast mass transfer of atrazine from the solution to adsorbent's surface/macropores as a result of flux/concentration gradient of the solute. Moreover, atrazine is more soluble in water than the fipronil. Rate of adsorption for both pesticides decreased with increase in time. Compared to atrazine adsorption of 62.77% (24 hr) and 70.40% (48 hr), the respective values for fipronil were 75.76 and 84.24% suggesting that fipronil was higher sorbed onto the STA. The kinetics data for atrazine and fipronil sorption was fitted to the pseudo first order (PFO), pseudo second order (PSO) and modified Elovich model using linear equations (Fig. 2) and the kinetics constants were calculated (Table 1). Results suggested that the data fitted best to the PSO model for sorption of both pesticides and the r^2_{Adj} values were 0.992 and 0.976 for the atrazine and fipronil, respectively. The PSO model suggests that the rate of adsorption is dependent more on the availability of adsorption sites than the concentration of pesticide in the solution[22] and higher pesticide adsorption at very low concentrations[23]. The intraparticle diffusion (IPD) plot

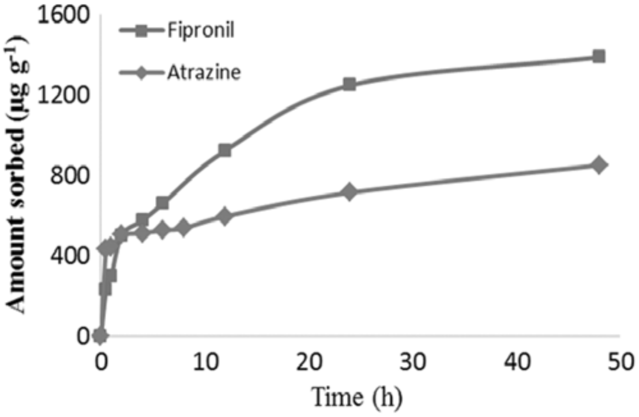

Fig. 1 — Kinetics of atrazine and fipronil adsorption onto the sugarcane trash ash (STA)

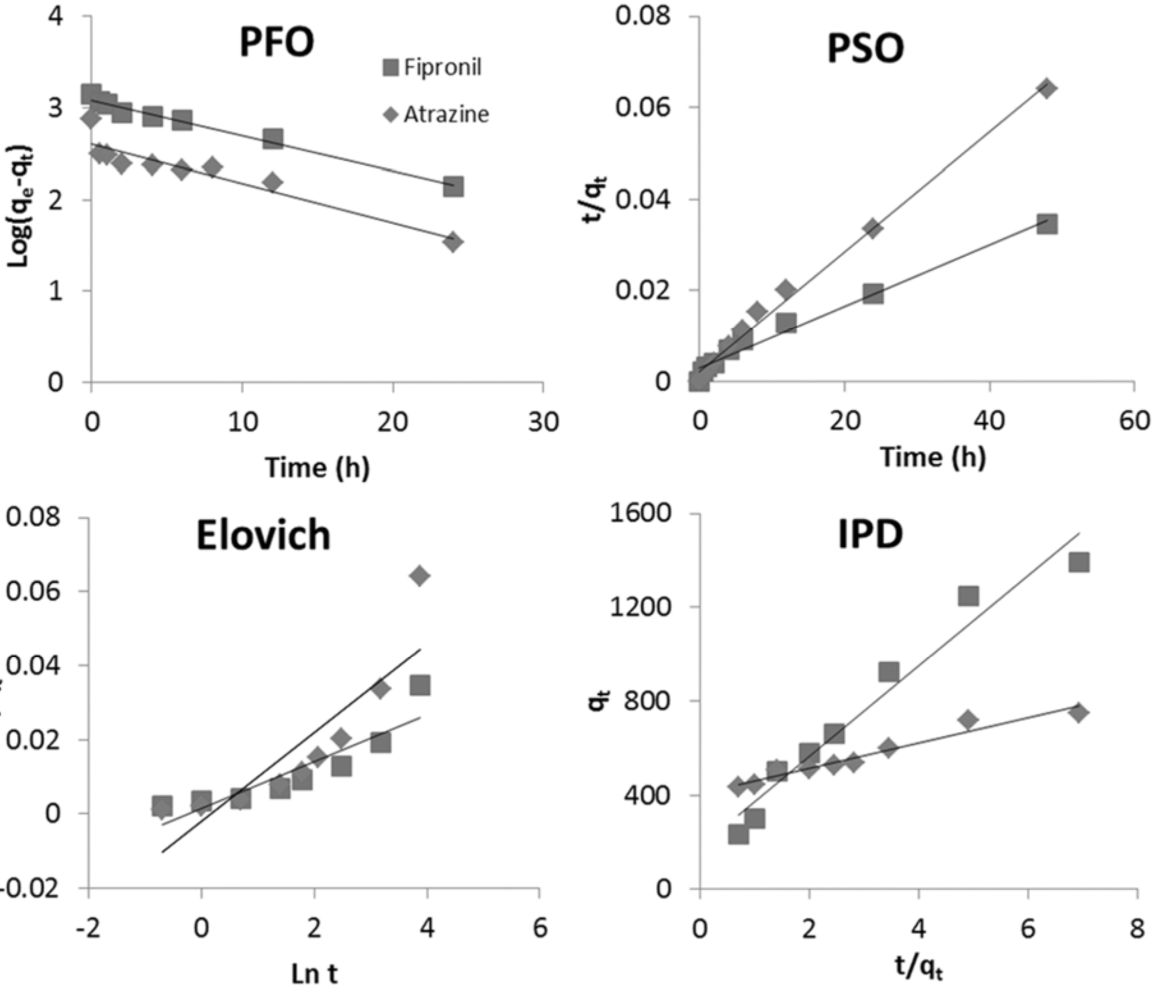

Fig. 2 — Plots of pseudo-first-order (PFO), pseudo-second order (PSO), modified Elovich and intra-particle diffusion models for atrazine and fipronil onto the sugarcane trash ash (STA). The q_t is the amount of pesticide sorbed ($\mu g\ g^{-1}$) at time 't'

Table 1 — Model parameters and r^2_{Adj} of the studied kinetic models for fipronil and atrazine in the sugarcane trash ash (STA)

Model	Parameter	Atrazine	Fipronil
Modified Elovich	α_E	21812.5	99.8
	β_E	84.0	158.7
	r^2_{Adj}	0.720	0.783
Pseudo-First Order	$q_{e,exp}$	750.0	1390.0
	$q_{e,calc}$	406.7	1216.2
	k_1	0.099	0.089
	r^2_{Adj}	0.855	0.984
Pseudo-Second Order	$q_{e,exp}$	750.0	1390.0
	$q_{e,calc}$	769.2	1428.6
	K_2	0.0008	0.0002
	r^2_{Adj}	0.992	0.976
Intra-Particle Diffusion	k_i	53.6	193.3
	C	406.2	178.4
	r^2_{Adj}	0.950	0.951

α_E (mg kg^{-1} min^{-1}); β_E (kg mg^{-1}); k_1 (min^{-1}); k_2 (kg mg^{-1} min^{-1}); k_i [(mg (kg $min^{0.5})^{-1}$]

(Fig. 2) lines for both pesticides did not pass through the origin indicating that the intraparticle diffusion was not the only rate controlling step and the boundary layer diffusion might have affected the adsorption to some degree. The value of the intercept in the IPD model gives an idea about the thickness of the boundary layer (Table 1). The boundary layer thickness can be defined as the distance from the adsorbent where the concentration of the diffusing species reaches 99% of the bulk concentration[24]. High thicknesses show higher adsorption capacities.[25] In general, adsorption is controlled by the intraparticle diffusion due to the microporosity of the adsorbent, which is in agreement with the findings that ash surfaces studied were mostly mesoporous in nature.

Adsorption-desorption studies

Adsorption of atrazine and fipronil onto the STA was studied at 1:250 and 1:2000 (ash: solution ratio), respectively. Different adsorbent:solution ratios were used so that pesticide adsorption lied in 30-85% range and was done to assure measurable amount of pesticide in solution. The concentration of atrazine varied between 5 to 25 mg L^{-1} while for fipronil it was 0.5-1.5 mg L^{-1}. Results suggested that adsorption of both the pesticides was dependent on their initial concentration in the solution and adsorption decreased with increase in the pesticide concentration (Table 2). The adsorption of atrazine onto the STA varied between 35.41-85.45% while for fipronil it was 38.79-62.41%. The partition coefficient (K_d) values for atrazine and fipronil adsorption ranged from 137.0-1445.3 and 1267.5-3321.1, respectively. The higher K_d values for the fipronil suggested higher adsorption and this can be it can be attributed to lower aqueous solubility and higher octanol-water partition coefficient of fipronil. Literature suggests that adsorption is negatively related to aqueous solubility and positively to the octanol-water partition coefficient[26].

The data for both pesticides adsorption was fitted to the linear form of the 2-components adsorption isotherms namely the Freundlich, the Langmuir and the Temkin isotherms (Fig. 3, Table 3). Fitting the adsorption data to the Freundlich isotherm observed the coefficient of determination (r^2) values >0.958 and r^2_{Adj} values >0.944 for both pesticides indicating the perfect fit of the observed data. The K_{Fads} values, which represent the adsorption at 1 mg L^{-1} concentration, were 1108.8 and 849.4 for atrazine and fipronil, respectively. However, due to different adsorbent:adsorbate ratio used for the atrazine and fipronil adsorption, comparison of parameter is not advisable. The $1/n_{ads}$ parameter, which represents the intensity of adsorption and effect of concentration on adsorption, suggested that adsorption of both pesticides was highly nonlinear and adsorption decreased with increase in concentration of solute. The 1/n values <1 suggested L-type adsorption isotherms.[27] The $1/n_{ads}$ values for the atrazine and fipronil were 0.23 and 0.407, respectively suggesting higher nonlinearity for atrazine adsorption. Due to highly nonlinear Freundlich adsorption isotherms parameter $K_{Fads}x1/n_{ads}$ was selected to compare adsorption of both pesticides on to the STA. The $K_{Fads}x1/n_{ads}$ values for the atrazine and fipronil were 253.18 and 345.71, respectively suggesting that fipronil was more sorbed onto the STA than atrazine. Fitting the data of atrazine and fipronil adsorption to the Langmuir adsorption isotherm suggested that the r^2 and r^2_{Adj} values for atrazine and fipronil were less than that observed for the Freundlich isotherm.

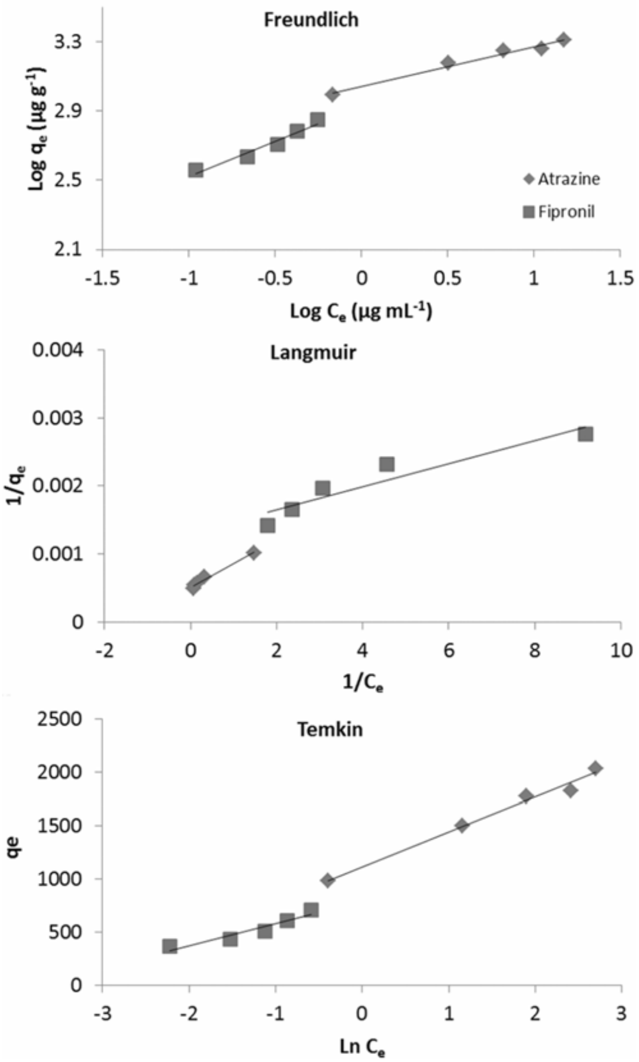

Fig. 3 — The Freundlich, the Langmuir and the Temkin isotherms for atrazine and fipronil adsorption on to the sugarcane trash ash (STA)

Table 2 — Parameters for atrazine and fipronil adsorption onto the sugarcane trash ash (STA)

Parameter	Atrazine (µg mL^{-1})					Fipronil (µg mL^{-1})				
	5	10	15	20	25	0.5	0.75	1.0	1.25	1.57
Percent adsorption	85.25	65.22	51.44	39.67	35.41	62.41	49.66	43.91	41.66	38.79
Partition coefficient (K_d)	1445.3	468.8	264.9	164.4	164.4	3321.1	1972.6	1565.6	1427.9	1267.5

However, maximum adsorption capacity (Q_0) of 769.2 and 2000 for atrazine and fipronil, respectively, suggested that the STA showed higher adsorption capacity for fipronil. The prediction of adsorption parameters for pesticide adsorption using the Temkin model (Table 3) suggested good fit of the observed data for atrazine (r^2_{Adj} = 0.982) adsorption, however fipronil data did not fit well (r^2_{Adj} = 0.885). The maximum binding affinity (A_{Tem}) parameter for the fipronil (45.04) was higher than that for atrazine (29.85) suggesting that the fipronil was more easily sorbed onto the STA. Thus, fitting adsorption data to three commonly used 2-parameter isotherms suggested that, in general, the Freundlich isotherm best explained the adsorption of both pesticides on to the STA. The STA has significant capacity to adsorb both pesticides.

Reversibility of adsorption plays an important role in determining the net amount remained sorbed. Desorption of both pesticides from the STA was studied at the lowest and the highest concentration after adsorption and 3 desorption cycles were performed. Results suggested that initial concentration of pesticide affected the amount of pesticide desorbed. Further, amount desorbed decreased with successive desorption cycle. Fipronil was less desorbed than the atrazine as no desorption was observed at lower concentration. Percent fipronil desorbed at higher concentration was 2.27%. The percent atrazine desorption from the STA was 4.83 and 9.32 at the lower and the higher concentration, respectively. The desorption data was fitted to the best fitted adsorption isotherm i.e. the Freundlich isotherm and graphs are presented in Fig. 4 while adsorption constant are shown in Table 4. The K_{Fdes} values for atrazine desorption were higher for desorption done at higher concentration (K_{Fdes} = 1757.1) than at lower concentration (K_{Fdes} = 979.94) suggesting that net amount of atrazine remain sorbed was more at higher concentration. The Freundlich $1/n_{des}$, which take into account the nonlinearity in the desorption isotherms, were lower than the $1/n_{ads}$ values for both pesticides suggesting hysteresis (H). The ratio of slope of desorption and adsorption $(1/n_{des})/(1/n_{ads})$ gives hysteresis (H) constant. A value of H < 1 indicates that the rate of desorption is slower than the rate of adsorption (positive hysteresis) while, H >1 indicate that rate of desorption is higher than rate of adsorption (negative hysteresis).[28] The H values

Table 3 — Constants for adsorption of atrazine and fipronil on to the sugarcane trash ash (STA)

Model	Parameters	Atrazine	Fipronil
Freundlich	K_{Fads}	1100.8	849.4
	$1/n_{ads}$	0.230	0.407
	r^2	0.981	0.958
	r^2_{Adj}	0.975	0.944
Langmuir	Q_0	769.2	2000.0
	K_L	6.50	1.25
	r^2	0.977	0.892
	r^2_{Adj}	0.970	0.855
Temkin	b_{Tem}	327.75	205.21
	A_{Tem}	29.85	45.04
	r^2	0.987	0.914
	r^2_{Adj}	0.982	0.885

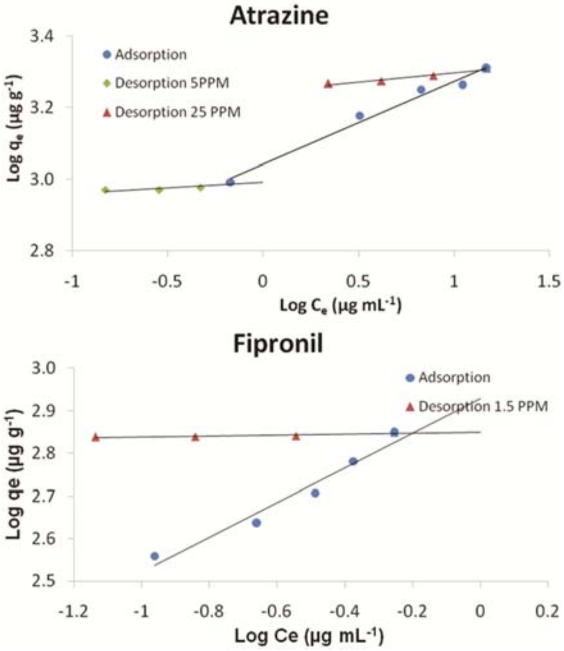

Fig. 4 — The Freundlich adsorption-desorption isotherms for atrazine and fipronil on to the sugarcane trash ash (STA)

Table 4 — Freundlich model parameters for desorption of atrazine and sulfosulfuron from the sugarcane trash ash

Treatment	Atrazine				Fipronil			
	K_f	1/n	r^2_{Adj}	H	K_f	1/n	r^2_{Adj}	H
Lower concentration	979.94	0.030	0.734	0.130	-	-	-	-
Higher concentration	1757.1	0.052	0.955	0.226	707.78	0.012	0.825	0.029

H (Hysteresis)- $1/n_{des}/1/n_{ads}$; ND- Not detected were 0.130 (lower concentration) and 0.226 (higher concentration) for atrazine and 0.029 for fipronil. The H values for atrazine were more at the higher pesticide concentration than at the lower concentration suggesting that hysteresis was more at the lower pesticide concentration. Further, hysteresis was more for the fipronil desorption than the atrazine suggesting that net amount retained was more for the fipronil.

Earlier studies have shown that plant biomass ashes show significant capacity for pesticides and porous nature of unburnt carbon materials in the ashes are responsible for pesticide adsorption.[21] The atrazine can interact both specifically (H-bonding and charge-transfer interactions) as well as non-specifically (hydrophobic-like interactions) with non-polar fraction of the adsorbent.[29] However, no information is available on sorption mechanism of fipronil in carbonaceous materials. The interactions between the carbon surface of the ash and functional groups (amino, sulfenyl, cyano) of fipronil as well hydrophobic interaction between nonpolar fraction of adsorbent and adsorbate might be paying a role in adsorption.

Conclusion

The study evaluated the kinetics and adsorption potential of the sugarcane trash ash (STA) for adsorb atrazine and fipronil. The pseudo second order model best explain the kinetics of pesticide's sorption. The STA show higher adsorption of fipronil than the atrazine and is attributed to the high surface area and porosity of the STA. The Freundlich models best explain the adsorption-desorption phenomenon. Thus, the STA can be used as a low cost adsorbent for removal of pesticides from water/waste water; thus, help in preventing environmental contamination caused by the pesticides.

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