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RESEARCH

Effect of soil amendments on the sorption behavior of atrazine in sandy loam soil

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Abstract The sorption behavior of pesticides applied during cultivation of crops is affected by amendments such as farm yard manure (FYM) and vermicompost (VC) during land preparation. Among pesticides, atrazine, a widely used herbicide in many crops, was analyzed for its kinetics and sorption behavior through the addition of FYM and VC in sandy loam soil. The pseudo-second-order (PSO) model best fit the kinetics results in the recommended dose of FYM and VC mixed soil. More atrazine was sorbed onto VC mixed soil than FYM mixed soil. In comparison to control (no amendment), both FYM and VC (1, 1.5, and 2%) increased atrazine adsorption, but the effect varied with dosage and type of amendment. The Freundlich adsorption isotherm adequately explained atrazine adsorption in soil/soil + (FYM/VC) mixtures, and the adsorption was highly nonlinear. The values of Gibb's free energy change (ΔG) were negative for both adsorption and desorption in soil/soil + (FYM/VC) mixtures, suggesting sorption was exothermic and spontaneous in nature. The results revealed that the application of amendments used by farmers interferes the availability, mobility, and infiltration of atrazine in the soil. Therefore, the findings of this study suggest that amendments such as FYM and VC can be effectively used to minimize the residual toxicity of atrazine-treated ago-ecosystems in tropical and sub-tropical regions.

Keywords Adsorption · Desorption · Triazine herbicide · Amendments · Models

Introduction

After the onset of "green revolution," usage of fertilizers, pesticides, and high-yielding varieties increased by many folds across the globe. To maintain the yield potential of such varieties, the use of pesticides, viz., insecticides, herbicides, fungicides, etc., has also been increased by many times (Ray, 2022). Among herbicides, atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) is a widely used pre- and early post-emergent selective and systemic triazine group of herbicide mainly used in controlling broadleaf and grassy weeds (Kumar & Singh, 2016). Due to its indiscriminate use over the years, a global problem of soil and water pollution has been raised because of its high chemical stability and significant

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toxicity to non-target organisms due to lipophilicity, leading to bio-accumulation and bio-concentration in the food chain (Urseler et al., 2022) and apparent mobility in soil and water (Douglass et al., 2015; Sánchez et al., 2017; Ferronato et al., 2018). The US Environment Protection Agency (USEPA) has declared atrazine a class III chemical, which signifies a "possible human carcinogen" and a moderately toxic chemical. The USEPA and the European Union have fixed the maximum contaminant level (MCL) of atrazine at 3.0 μg L^{-1} and below 0.1 μg L^{-1} in drinking water (Anonymous, 2009). Atrazine is also a potential endocrine disruptor in vertebrates (Lasserre et al., 2009) and lethal to fish (Jiya et al., 2001) and causes hermaphroditism in amphibians, mainly frogs (Hayes, 2004; Hayes et al., 2003; Sass & Colangelo, 2006). In humans, in vitro exposure to atrazine causes an increase in aromatase activity in adrenocortical carcinoma cells (Sanderson et al., 2002) and also has the potential to cause birth defects, low birth weights, and menstrual problems when exposed at concentrations above the Federal standard (0.1 mg kg^{-1}) (Duhigg, 2009).

The sorption behavior of atrazine in soil is an important parameter for determining groundwater contamination potential and bioavailability. In various environmental ecosystems, sorption generally decreases the amount of adsorbate in the aqueous phase. Factors that influence atrazine sorption onto soil include clay content (Wahid & Sethunathan, 1978), organic matter (Cox et al. 1997; Jain & Singh, 2018), soil moisture content, soil temperature, structure, and nature of pesticide (Dragun, 1998). Atrazine being a weak base (pKa-1.68) behaves like a neutral species at pH level higher than the dissociation constant pH (House, 1998). Also, its adsorption decreases with increasing pH (Liu et al., 1995). However, with respect to organic carbon content, adsorption is positively correlated (Swarcewicz & Skoersk, 2007; Wang & Keller, 2009). Adsorption of atrazine onto soil alone is generally poor when compared with externally added adsorbent material (Ahmad & Rahman, 2009; Sun et al., 2019; Yue et al., 2017). In the soil, organic carbon content and physical bonding with clay minerals such as quartz or geolite play an important role in the sorption of atrazine onto the soil (Martins et al., 2018). There are reports available on biochar made from various materials such as tree wood (Lima et al., 2022), peanut shell (Wang et al., 2020), Australian pine, Brazilian pepper, coconut husk, cypress, loblolly pine, pecan shell feedstocks (Gaffar et al., 2021), rice straw (Mandal et al., 2021), modified fallen leaf (Cao et al., 2021), and many more matrices that are used for enhancing the adsorption of atrazine from soil and water systems. Due to the high usage of atrazine in sugarcane crop, sugarcane trash ash or sugarcane top-derived biochars are also being used to enhance atrazine sorption in the soil (Huang et al., 2018; Yadav & Singh, 2021). Nano metal oxides such as nickel oxide (NiO), zinc oxide (ZnO) (Allam et al., 2021), and magnesium oxide (MgO) were also used for the sorption of atrazine from soil and water matrices. But these methods require sophisticated costly equipment and skilled professionals leading to higher production cost and the deterioration of environmental quality. The use of such methods has become less popular among farmers as a result of the combined effect of the factors listed above, whereas the addition of manures such as FYM and VC to soil is a practice followed by our farmers for a long time during field preparation (Gogoi et al., 2021). The incorporation of organic matter into the soil increases adsorption and decreases desorption of herbicides used during crop production (Moreau and Mouvet, 1997; Abate et al., 2004; Lima et al., 2010).

Atrazine is a popular herbicide in maize, sorghum, sugarcane, and other crops and is applied as a pre- and early-post emergence. It is very harmful to non-target biotic and abiotic components of the ecosystem. The herbicide has high potential to leach out to ground water, thus contaminating them. The leaching of atrazine is reduced through addition of various amendments in the soil system via adsorption process. Therefore, it is critical to understand the fate of atrazine in the soil system, as very fewer studies have been conducted so far to investigate the influence of organic amendments on fate of atrazine (Lima et al., 2010) in the soil ecosystem. Thus, the specific purpose of this study was to find out locally available, cheap, and eco-friendly organic amendments like FYM and VC in reducing harmful effects of atrazine in the soil ecosystem.

Materials and methods

Atrazine

Atrazine (6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine) having CAS number 1912–24-9 of analytical grade {95% purity; vapor pressure 3.85×10^{-2} mPa at 25 ℃; specific gravity 1.23 at 22℃; octanol water coefficient (K_{OW}) 2.5 at 25 ℃; pKa 1.68 (very weak base); solubility 33 mgL^{-1} in water at pH 7 and at 22 ℃ 24 g L^{-1} in ethyl acetate, 31 gL^{-1} acetone, and 28 gL^{-1} in dichloromethane} was purchased from Rallis India Ltd., Bangalore, India. Chemicals and solvents of analytical grade were purchased locally.

Soil, farmyard manure, and vermicompost

The soil (Typic Haplustepts, Alfisol) was collected in the autumn season of 2021 from the Central Research Farm of ICAR-Indian Grassland and Fodder Research Institute, Jhansi, Uttar Pradesh, India (ICAR-IGFRI) (25°31′1″ N 78°31′34″E) at a depth of 0–15 cm. After collecting the soil, initial moisture content (14.8%) was estimated through gravimetric method and dried in shade under room temperature (25 ± 2℃) until the constant weight was achieved (5 days). Furthermore, the soil was ground, sieved through a 2-mm sieve, and stored in PTFE containers at room temperature. Farmyard manure (FYM) and vermicompost (VC) obtained from ICAR-IGFRI, Jhansi, were also room-dried at an average temperature of 25 ± 2 ℃ for 8 days, ground, and sieved through a 2-mm sieve and stored in PTFE containers at room temperature (25 ± 2℃). The physico-chemical properties of the soil and amendments (FYM and VC) were determined using standard analytical procedures presented in Table 1.

Kinetic studies

The kinetics of atrazine onto soil/soil + (FYM/VC) was studied using the batch sorption method under laboratory conditions with temperature and relative humidity of 25 ± 2℃ and 45 ± 2%, respectively (Mandal et al., 2017; Kumar and Singh, 2020). In brief, 5 g of soil mixed with amendment (1% FYM/VC) was taken in a 50-mL PTFE oak ridge tube. Each tube was then filled with 10 mL of 5 µg mL^{-1} atrazine in an aqueous 0.01 M $CaCl_2$ solution and equilibrated for different time periods, namely 0, 15, 30, 1, 2, 4, 8, 12, 24, and 48 h. After equilibration, the soil suspension was centrifuged using a Remi C24 centrifuge at 1396 × g for 5 min. Herbicide residues in the supernatant were quantified using high-performance liquid chromatography (HPLC) after filtration with a 0.45µ PTFE syringe filter. The amount of atrazine adsorbed by the sorbent was estimated using the difference between the initial and final concentrations of atrazine in the supernatant. On the basis of the mass balance calculation, it was concluded that there was no sorption of atrazine on the tube surface, and it was stable

Table 1 Physio-chemical properties of soil, FYM, and VC

Properties	Soil	FYM	VC	Method (reference)
Textural class	Sandy loam	-	-	USDA triangular diagram method
Sand (%)	58	-	-	Hydrometer method (Bouyoucos, 1927)
Silt (%)	30	-	-	
Clay (%)	12	-	-	
pH	7.4	7.04	7.82	Glass electrode pH meter (Jackson, 1967)
EC (dSm^{-1})	0.18	3.43	6.21	Digital conductivity meter (Jackson, 1967)
OC%	0.65	16.4	18.4	Wet digestion method (Walkley & Black, 1934)
N	184 kg/ha	0.76%	2.66%	Kjeldahl method (Bremner, 1965)
P	14.8 kg/ha	0.25%	1.78%	Olsen method (Olsen et al., 1954)
K	240.3 kg/ha	589.4 mg kg^{-1}	960.2 mg kg^{-1}	Atomic adsorption spectrophotometer (Wright & Stuezynski, 1996)
Ca (%)	1.1	2.6	2.5	
Mg (%)	1.6	1.4	2.95	
Fe (mg kg^{-1})	1128	2146	2486	
Zn (mg kg^{-1})	984.8	112.2	200.1	
Cu (mg kg^{-1})	56.4	48	36.4	
Mn (mg kg^{-1})	78.8	220.25	366.42	

during the equilibration period. The whole experiment was done in triplicate, and soil alone (without amendment) was treated as the control. Furthermore, for significance of the treatments, kinetics data was statistically analyzed (univariate linear model) using IBM SPSS Statistics for Windows.

Adsorption–desorption studies

The batch slurry method, as described in OECD Guidelines 106 (OECD, 2000), was used for the adsorption study of atrazine under laboratory conditions with temperature and relative humidity of 25 ± 2℃ and 45 ± 2%, respectively. In brief, a 1:2 soil:solution of atrazine was used for the adsorption study, and this ratio was selected so that adsorption of the herbicide will be in the range of 35–75%. Sandy loam soil sample (5 g, oven dry basis) and herbicide in aqueous 0.01 M $CaCl_2$ (10 mL) at different concentrations of atrazine (2, 4, 6, 8, and 10 μg mL^{-1}) were taken in a 50-mL PTFE oak ridge tube. To investigate the effect of the amendment on adsorption, soil samples were supplemented with 1, 1.5, and 2% of FYM and VC, respectively. These levels correspond to recommended dosages of 10 (1%), 15 (1.5%), and 20 (2%) t ha^{-1} of soil, respectively. The whole experiment was done with three replicates, with one each of without soil and without herbicide which was treated as a control. Tube-containing samples were equilibrated on an orbital shaker for 24 h at room temperature. After equilibration, the soil suspension was centrifuged at 1396 × g for 5 min, and atrazine residue was quantified using HPLC after filtration with a 0.45μ PTFE syringe filter. The amount of atrazine adsorbed by the soil/soil + amendment mixture was calculated from the initial and final concentration differences of atrazine in the supernatant.

After completion of adsorption, the same tube of only highest and lowest concentration was used for desorption study. From each tube, a total of 7 mL of supernatant was replaced with the same amount of fresh 0.01 M $CaCl_2$ solution and again shaken for 24 h to attain equilibrium. The soil suspension was centrifuged, and 7 mL of the supernatant was replaced with fresh 0.01 M $CaCl_2$ solution. Each sample was subjected to three cycles in order to calculate three times the rate of serial desorption. The residues of herbicide were calculated after each cycle of desorption, and further desorption from soil or soil + amendment was calculated. For determining the significance among treatments, both adsorption and desorption data were statistically analyzed (univariate linear model) using IBM SPSS Statistics for Windows.

High-performance liquid chromatography (HPLC) analysis

A high-performance liquid chromatography (Young Ling 9100 HPLC System) was used with a vacuum degasser, binary pump, and photodiode array (PDA) detector and a reverse phase Chromatopak 30 cm C-18 stainless steel column [250 mm × 4 mm (i.d.)], acetonitrile: 0.1% aqueous o-phosphoric acid (70:30) as a mobile phase, at a flow rate of 1 mL min^{-1} at wavelength of 222 nm, and the column temperature was maintained at 40℃ as per the earlier reported method of Kumar and Singh (2016). The limit of detection (LOD) and limit of quantification (LOQ) were 0.06 and 0.10 mg mL^{-1}, respectively. The standard curve when plotted in the range of 0.1–10 mg L^{-1} showed linearity with R^2 (correlation coefficient) value 0.997.

Kinetic models

Experimental kinetics data were fitted to linear form of the Lagergren pseudo-first-order (PFO) (Lagergren, 1898), pseudo-second-order (PSO) (Ho & McKay, 1999), modified Elovich (Chien & Clayton, 1980), and intra-particle diffusion (IPD) (Weber & Morris, 1963) models. These models illustrate the mechanism of adsorption and potential rate controlling steps such as chemical reactions, diffusion, or mass transfer (Gücek et al., 2005; Sadeek et al., 2015).

$$\text{PFO}\ \log\left\{q_e - q_t\right\} = \log q_e - \left\{\frac{K_1}{2.303}\right\}t \tag{1}$$

$$\text{PSO}\ \frac{t}{qt} = \frac{1}{\mathrm{K2qe2}} + \left\{\frac{1}{\mathrm{qe}}\right\}t \tag{2}$$

$$\text{Modified Elovich}\ qt = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{3}$$

$$\text{IPD}\ qt = \left[K\mathrm{int} \times t\exp\left(\frac{1}{2}\right)\right] + C \tag{4}$$

where K_1 (h^{-1}) and K_2 (kg mg h^{-1}) are Lagergren pseudo-first-order and pseudo-second-order rate constants, respectively; α and β are initial sorption rate (mg Kg^{-1} h^{-1}) and desorption constants (kg mg^{-1}); C and K_{int} are intercept and intra-particle diffusion rate constants (mg kg^{-1} $h^{-1/2}$). The boundary conditions for time were $t=0$ to $t=t$ whereas for amount sorbed was $q_t=0$ to $q_t=q_t$. q_e (mg kg^{-1}) and q_t (mg kg^{-1}) were the amounts of herbicide adsorbed at equilibrium and at time *t*, respectively.

Adsorption models

Adsorption isotherm models reveal the interaction between adsorbate and adsorbent. They are an important tool in optimizing the use of adsorbents. They play a significant role in predicting the operation of adsorption systems by correlating the equilibrium values either by theoretical or empirical equations. Thus, experimental adsorption data were fitted to the linear form of most common adsorption isotherms, viz., Freundlich (Freundlich, 1906), Langmuir (Langmuir, 1916), and Temkin (Temkin & Pyzhev, 1940) isotherm models. Freundlich model deals with both mono- and multilayer with homo- and heterogeneous surfaces. Also according to this model, adsorption energies are reduced exponentially after completion of adsorption process. Langmuir model deals with the relationship of adsorbate and number of active sites present in the adsorbent. According to this model, adsorbate is taken up at a fixed number of definite sites, and after achieving the equilibrium, no further adsorption is possible. All the sites are energetically equal without any interface between adsorbate molecules. Temkin model deals with adsorbate and adsorbent interactions. According to this model, adsorption heat is decreased linearly for all adsorbate molecules. The uptake of adsorbate is also controlled by

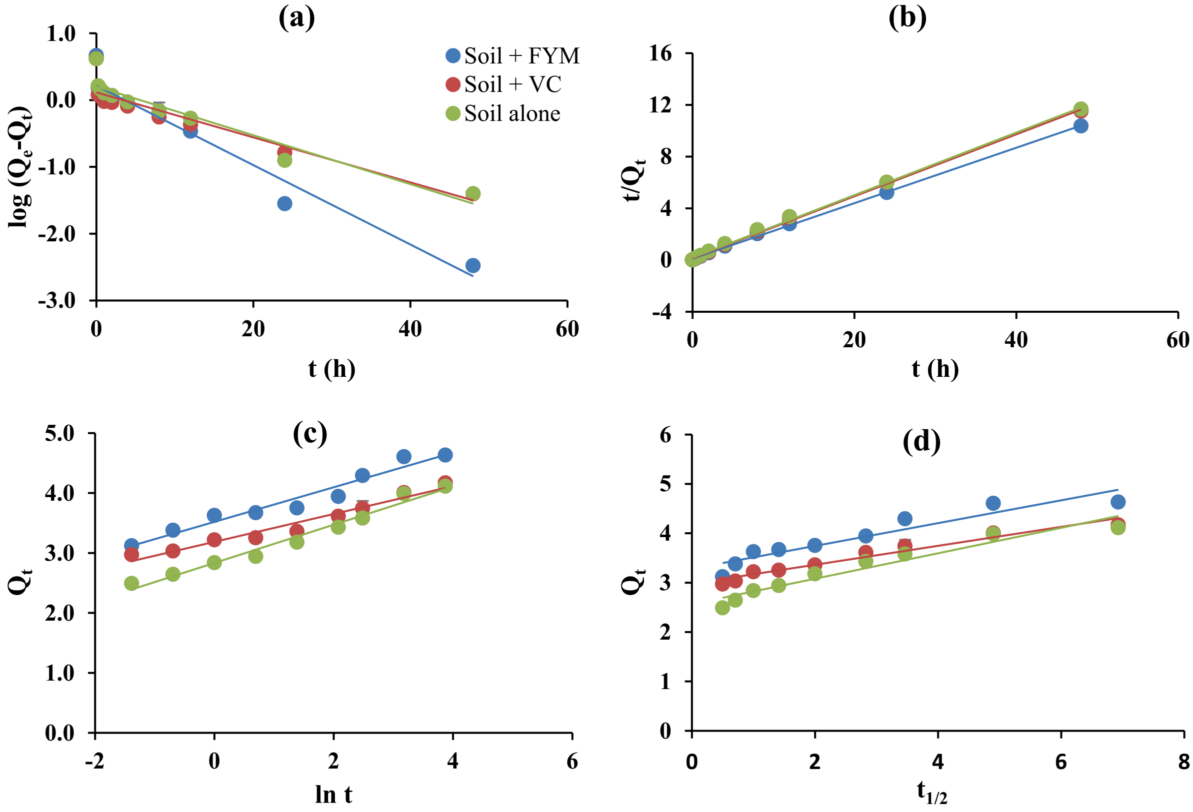


Fig. 1 Linear plots of pseudo-first-order (**a**), pseudo-second order (**b**), modified Elovich (**c**), and intra-particle diffusion (**d**) models for atrazine in control, 1% each of FYM and VC mixed sandy loam soil

Table 2 Rate constants K_1 (min^{-1}), K_2 (kg mg^{-1} min^{-1}), model parameters, and r^2_{Adj} of the studied kinetic models for atrazine in soil alone, soil + 1% FYM, and soil + 1% VC

		Adsorbent		
Models	Parameters	Soil alone	Soil + 1% FYM	Soil + 1% VC
Pseudo-first-order	$Q_{e\ \text{exp}}$	2.196	1.477	2.187
	$Q_{e\ \text{cal}}$	1.598	1.638	1.301
	K_1	0.084	0.137	0.078
	$r^2_{\ \text{adj}}$	0.903	0.943	0.869
	RMSE*	0.164	0.200	0.178
Pseudo-second-order	$Q_{e\ \text{exp}}$	2.196	1.477	2.187
	$Q_{e\ \text{cal}}$	4.134	4.664	4.174
	K_1	0.321	0.409	0.415
	$r^2_{\ \text{adj}}$	0.998	0.999	0.999
	RMSE	0.080	0.104	0.078
Modified Elovich	α_E	0.413	0.348	0.275
	β_E	3.137	3.466	4.305
	$r^2_{\ \text{adj}}$	0.977	0.951	0.958
	RMSE	0.143	0.095	0.177
Intra-particle diffusion	K_i	0.258	0.231	0.192
	C	2.565	3.282	2.980
	$r^2_{\ \text{adj}}$	0.921	0.873	0.947
	RMSE	0.141	0.164	0.085
F_{AT}	10,810 ($P < 0.0001$)			
F_{T}	9435 ($P < 0.0001$)			
$F_{\text{AT} \times \text{T}}$	41.783 ($P < 0.0001$)			

*$RMSE$ root mean square error, AT amendment type, T time. F values determined using SPSS software through univariate two-way ANOVA. P values denote degree of significance. All treatments significantly differed at $P < 0.05$, when post hoc test performed with Tukey's HSD

adsorbate and adsorbent relations (Ali et al, 2016; Chang & Juang, 2004; Yu et al., 2020).

$$\text{Freundlich model}\ \log\ qe = \log\ K\text{F} + \frac{1}{n}\log Ce \tag{5}$$

$$\text{Langmuir model}\ \frac{1}{q_e} = \frac{1}{Q0} + \frac{1}{Q0bLCe} \tag{6}$$

$$\text{Temkin model}\ q_e = B\ln A\text{Tem} + B\ln C\text{e} \tag{7}$$

where q_e (mg kg^{-1}) is the amount of herbicide sorbed, C_e (mg L^{-1}) is the herbicide concentration in the solution at equilibrium; K_F and $1/n$ are Freundlich adsorption constants; Q_0 (L mg^{-1}) and b_L (mg g^{-1}) are Langmuir constants; A_Tem (Lg^{-1}) is the binding constant for Temkin isotherm equilibrium; B (J mol^{-1}) is a constant which is associated with heat of adsorption/desorption and $B = \text{RT}/\text{b}_\text{Tem}$ [R is universal gas constant (8.314 JK^{-1} mol^{-1}); T (K) is the temperature; and b_Tem is the Temkin isotherm constant].

Results and discussion

Kinetic studies

Adsorption kinetics is one of the important parameters that controls adsorption rate and adsorption efficiency of adsorbate. They are very valuable when revealing with fate of atrazine in the soil system (Yu et al., 2020). The kinetics of atrazine was studied in 1% FYM/VC mixed sandy loam soil. Results showed that during half an hour of shaking 29.74%, 39.45%, and 36.20% of atrazine were adsorbed onto control, FYM, and VC amended soil, respectively (Supplementary Table A). The kinetics results clearly showed that as shaking time increased, the amount of herbicide adsorption increased, but the rate of adsorption decreased. At 24 h of shaking, 37.95%, 44.65%, and 47.80% of the atrazine applied in the solution were adsorbed by control, FYM, and VC amended soil, respectively, which remained almost constant at

Table 3 Percentage of atrazine adsorbed in FYM, VC amended sandy loam, and control soil and the parameters' estimates of the three adsorption models applied, Freundlich, Langmuir, and Temkin isotherm

Adsorbent								
Models	Parameters	Soil alone	Soil + 1% FYM	Soil + 1.5% FYM	Soil + 2% FYM	Soil + 1% VC	Soil + 1.5% VC	Soil + 2% VC
Adsorption %		30.14–38.51	30.28–45.63	34.21–49.76	30.28–45.63	37.67–46.47	29.32–44.42	36.20–45.68
Freundlich isotherm	K_F	0.951	1.086	1.290	1.633	1.254	1.611	1.985
	$1/n_{\mathrm{Fads}}$	1.121	1.225	1.423	1.813	1.332	1.581	2.439
	ΔG	−0.055	−0.091	−0.095	−0.540	−0.249	−0.212	−0.276
	r^2_{Adj}	0.954	0.941	0.918	0.987	0.929	0.950	0.949
	RMSE*	0.093	0.069	0.045	0.063	0.034	0.039	0.042
Langmuir isotherm	Q_0	10.482	7.294	5.324	23.644	10.661	0.568	15.08
	b_L	0.077	0.120	0.165	0.064	0.103	0.265	0.073
	r^2_{Adj}	0.920	0.939	0.906	0.940	0.934	0.856	0.939
	RMSE	0.084	0.093	0.088	0.073	0.074	0.064	0.088
Temkin isotherm	b_{Tem}	8696	10,379	14,087	10,841	12,466	14,751	9339
	A_{Tem}	0.809	0.502	1.628	0.060	0.758	59.310	0.212
	B	0.292	0.244	0.180	0.234	0.203	0.172	0.272
	r^2_{Adj}	0.995	0.987	0.859	0.896	0.830	0.972	0.938
	RMSE	0.076	0.088	0.101	0.097	0.085	0.077	0.056
F_{IC}	3364 ($P < 0.0001$)							
F_{AT}	29.384 ($P < 0.0001$)							
F_{AP}	17.551 ($P < 0.0001$)							
$F_{\mathrm{IC \times AT}}$	25.604 ($P = 0.0001$)							
$F_{\mathrm{IC \times AP}}$	3.822 ($P < 0.0001$)							
$F_{\mathrm{AT \times AP}}$	53.002 ($P < 0.0001$)							
$F_{\mathrm{IC \times AT \times AP}}$	3.925 ($P = 0.0001$)							

**RMSE* root mean square error, *IC* initial concentration, *AT* amendment type; *AP* amendment %. *F* values determined using SPSS software through univariate two-way ANOVA. *P* values denote degree of significance. All treatments significantly differed at $P < 0.05$, when post hoc test performed with Tukey's HSD

48 h of shaking (Supplementary Table A). So, it was concluded that at 24 h of shaking equilibrium was achieved. When compared with FYM amended soil, VC amended soil has a higher adsorption of atrazine. Atrazine is hydrophobic and has low surface tension or surface energy (dispersive); hence, increasing OC% will increase the adsorption of atrazine to the surface. In other words, any amendments or treatments that increase OC% on the surface that result in low surface energy will increase atrazine adsorption onto the surface. However, other factors such as pH, temperature, and salt concentration will likely affect the extent of the response (Lima et al., 2010).

Atrazine adsorption kinetics data were fitted to linearized forms of the pseudo-first-order (PFO), pseudo-second-order (PSO), modified Elovich, and intra-particle diffusion models, and different constants were calculated (Fig. 1 and Table 2). Among the three kinetics models, PSO model was best fitted to atrazine adsorption temporal kinetics as adjusted correlation coefficient r^2_{Adj} values (control: 0.998; FYM amended: 0.999; and VC amended: 0.999) were highest and root means square error (RMSE) was lowest (control: 0.080; FYM amended: 0.104; and VC amended: 0.078) for the PSO model. The best-fitting PSO model proposes that the rate of herbicide adsorption is more dependent on the availability of the site of adsorption than the concentration of herbicide in the solution (Njoku & Hameed, 2011). The IPD graphs did not pass through the origin, suggesting both intra-particle and boundary layer diffusion played a significant role in atrazine's adsorption (Cheung et al., 2007). The phenomenon of boundary layer diffusion

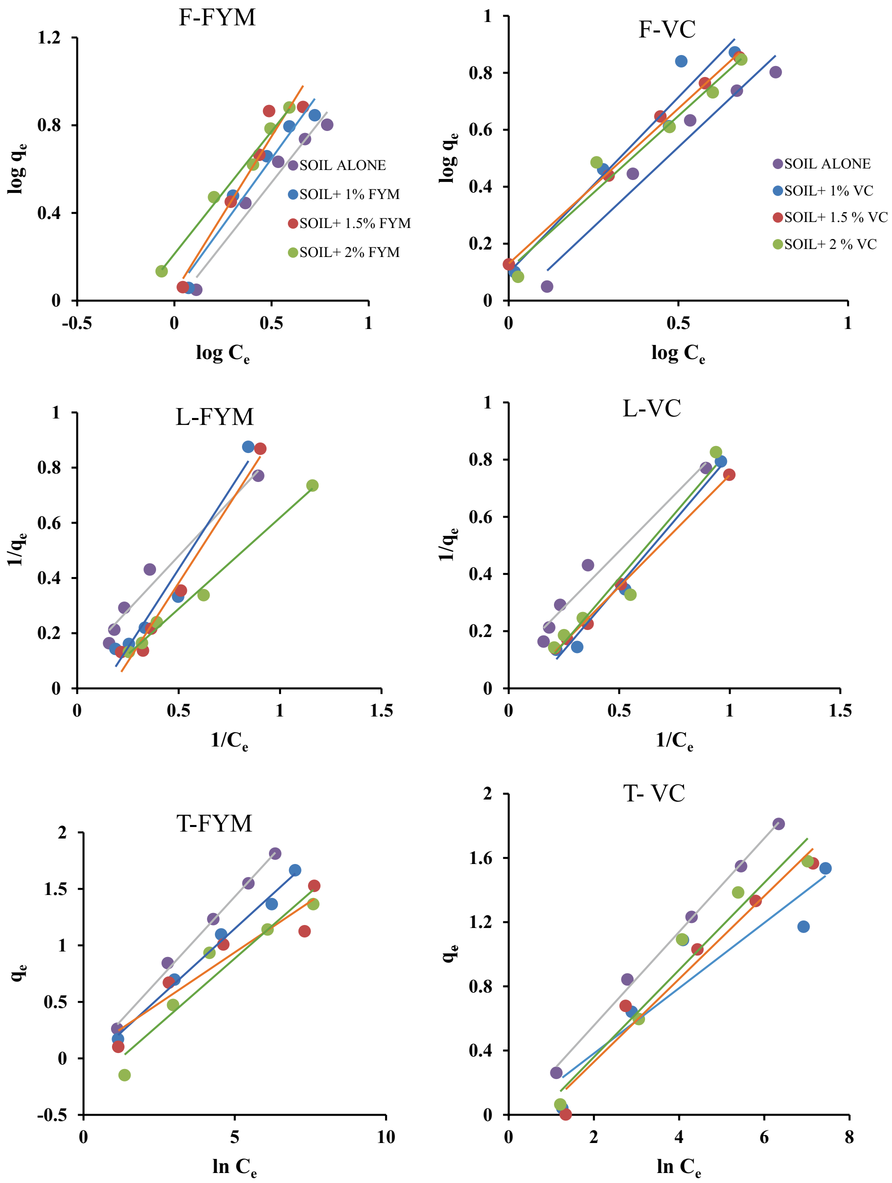


Fig. 2 Adsorption isotherms for atrazine adsorption in the farm yard manure (FYM) and vermicompost (VC) mixed soil [F, Freundlich; L, Langmuir; T, Temkin isotherm]

occurs when the rate of mass transfer differs during the initial and final phases of adsorption (Igwe et al., 2009). The porous nature of amendment particles is also attributed to intra-particle diffusion.

Adsorption desorption studies

To understand the behavior of interaction between atrazine and soil and also to reveal the sorption mechanism, adsorption isotherms are quantitatively established to determine the atrazine transfer phenomenon from solid phase to liquid phase and vice versa (Kasozi et al., 2012). The effect of FYM and VC on the adsorption of atrazine was studied in sandy loam soil. Results (Table 3) revealed that adsorption was slightly higher in VC amended soil than in FYM amended soil, and as the amount of amendment increases in the soil, the adsorption % also increases. Adsorption ranges from 30.14 to 38.51% for control soils, whereas adsorption ranges from 30.28 to 45.36%, 34.21 to 29.76%, and 30.28 to 45.63% for 1, 1.5, and 2% FYM amended sandy loam soils, respectively. Adsorption percent values for 1, 1.5, and 2% VC amended sandy loam soil were 37.67–46.47%,

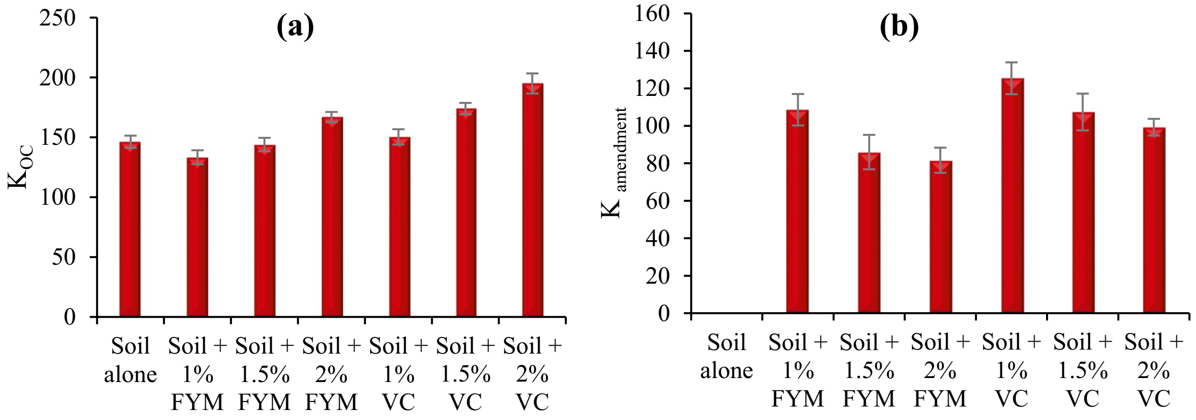
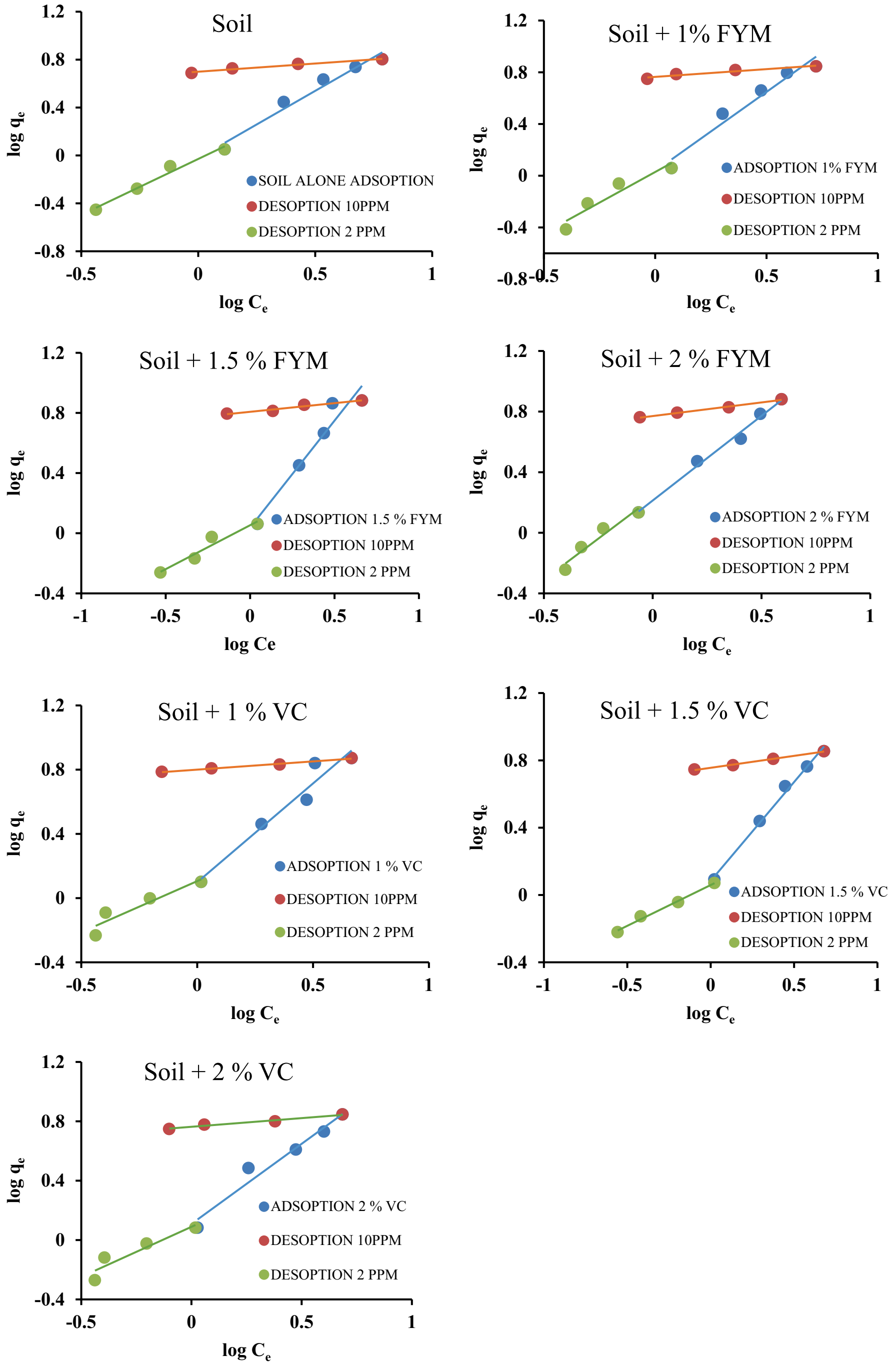


Fig. 3 Comparison of **a** K_{OC} (organic carbon normalized constant) and **b** $K_{\mathrm{Amendment}}$ [farm yard manure (FYM) and vermicompost (VC) content normalized constant]

29.32–44.42%, and 36.20–45.68%, respectively. All treatments were significantly different at $P < 0.05$, when post hoc test performed with Tukey's HSD (Table 3). Adsorption data for both amendments in soil were fitted to the linearized form of the Freundlich, Langmuir, and Temkin isotherms (Fig. 2), and constants were calculated. On the basis of higher r^2_{Adj} values (control: 0.954; 1, 1.5, and 2% FYM amended: 0.941, 0.918, and 0.987, respectively; and 1, 1.5, and 2% VC amended: 0.929, 0.950, and 0.949, respectively) and lower RMSE values (control: 0.093; 1, 1.5, and 2% FYM amended: 0.069, 0.049, and 0.063, respectively; and 1%, 1.5%, and 2% VC amended: 0.034, 0.039, and 0.042, respectively) among all three fitted models, the best-fitted model was Freundlich adsorption isotherm model (Table 3).

The K_{Fads} (a measure of pesticide adsorption at equilibrium concentration) values for control (no amendment), 1, 1.5, and 2% FYM mixed sandy loam soil were 0.951, 1.086, 1.290, and 1.633 $\mathrm{mg}^{1-\mathrm{nF}}\mathrm{kg}^{-1}\mathrm{L}^{\mathrm{nF}}$, respectively, whereas the values of K_{Fads} for 1, 1.5, and 2% VC mixed sandy loam soil were 1.254, 1.611, and 1.985 $\mathrm{mg}^{1-\mathrm{nF}}\mathrm{kg}^{-1}\mathrm{L}^{\mathrm{nF}}$, respectively (Fig. 2 and Table 3). As a result, with increasing the amount of amendment in the soil, the value of K_{Fads} increased. According to this study, the use of FYM and VC as soil amendments is effective for atrazine adsorption. The higher amount of atrazine adsorption in VC-amended soil may be due to the higher OC% (Ahangar et al., 2008; Fernández-Bayo et al., 2009). The values of $1/n_F$ which is a measure of the intensity of adsorption were 1.121 for control, and 1.225, 1.423, and 1.813 for 1, 1.5, and 2% FYM amended soil, respectively, whereas for 1%, 1.5%, and 2% VC-amended soil values, they were 1.332, 1.581, and 2.439, respectively. The values of $1/n_F$ being > 1 suggest an S-type adsorption isotherm in which increasing the concentration of atrazine in the solution increases adsorption (Kumar & Singh, 2020). Furthermore, the values of $1/n_F$ shifted away from unity, indicating an increase in the nonlinearity of adsorption isotherms in both amendments. Because of the highly nonlinear nature of atrazine adsorption in both amendments, $K_F.1/n_F$ was considered a constant for comparing adsorption for different treatments. The values of $K_F.1/n_F$ for control, 1, 1.5, and 2% FYM amendment were 1.066, 1.330, 1.836, and 2.961 respectively. Similarly, these values were 1.670, 2.547, and 4.841 for 1, 1.5, and 2% VC amendment, respectively. These results suggested that the effect of VC on the sorption of atrazine was higher than the effect of FYM (Kumar & Singh, 2020). Increased atrazine adsorption onto amendment mixed soil is attributed to an increase in OC content, leading to increased organic carbon normalized constant ($K_{\mathrm{OC}} = K_F \times 100/\%\mathrm{OC}$) values (Fig. 3). Compared to control, the values of K_{OC} were 1.21 and 1.33 times higher for the 2% FYM and VC amendments, respectively. This effect can be attributed to the clay content of the soil masking the surfaces of the amendment, resulting in a decrease in the normalized content of the amendment ($K_{\mathrm{amendment}} = K_F \times 100/\%$ amendment) with an increasing amendment.

Fig. 4 Freundlich isotherms for atrazine desorption from sandy loam soil/sandy loam soil + (FYM/VC)



The desorption of herbicides plays an important role in determining the mobility of herbicides in the soil profile. Atrazine was easily desorbed from the control soil, but the addition of an amendment reduced the amount of desorption. The Freundlich constants for desorption (K_{Fdes}) were higher at higher concentrations than at lower concentrations suggesting that a higher amount of atrazine was sorbed at higher concentrations (Fig. 4; Table 4). The Freundlich $1/n_{\mathrm{des}}$ values, which denote nonlinearity in the desorption isotherms, were lower than $1/n_{\mathrm{ads}}$ values with hysteresis. The slope of the desorption and

Table 4 Freundlich parameters for desorption of atrazine from soil/(FYM/VC) mixed sandy loam soil

		K_F	$1/n_{\mathrm{Fdes}}$	ΔG	r^2_{Adj}	H	RMSE*
Control	Higher	1.175	0.137	−0.177	0.971	0.122	0.083
	Lower	0.934	0.932	−0.075	0.968	0.832	0.097
1% FYM	Higher	4.825	0.120	−1.938	0.917	0.098	0.076
	Lower	1.069	0.947	−0.073	0.873	0.773	0.084
1.5% FYM	Higher	5.125	0.115	−2.048	0.944	0.081	0.076
	Lower	1.414	0.584	−0.135	0.913	0.411	0.079
2% FYM	Higher	5.643	0.180	−1.954	0.991	0.161	0.058
	Lower	1.704	0.680	−0.587	0.914	0.967	0.096
1% VC	Higher	5.698	0.103	−2.029	0.986	0.083	0.071
	Lower	1.146	0.636	−0.266	0.838	0.516	0.049
1.5% VC	Higher	6.023	0.142	−1.916	0.993	0.058	0.058
	Lower	1.356	0.485	−0.150	0.987	0.199	0.076
2% VC	Higher	6.310	0.117	−1.935	0.964	0.108	0.044
	Lower	1.486	0.674	−0.226	0.832	0.624	0.078
F_{AT}		0.664 ($P=0.0417$)		F_{AP}		3.812 ($P=0.026$)	
F_{IC}		4083 ($P<0.0001$)		F_{CN}		1144 ($P<0.0001$)	
$F_{\mathrm{AT\times AP}}$		1.219 ($P=0.0301$)		$F_{\mathrm{AT\times IC}}$		0.806($P=0.0372$)	
$F_{\mathrm{AT\times CN}}$		3.975 ($P=0.022$)		$F_{\mathrm{AP\times IC}}$		0.803 ($P=0.0451$)	
$F_{\mathrm{AP\times CN}}$		3.560 ($P=0.010$)		$F_{\mathrm{IC\times CN}}$		495.8 ($P<0.0001$)	
$F_{\mathrm{AT\times AP\times IC}}$		3.100 ($P=0.049$)		$F_{\mathrm{AT\times AP\times CN}}$		1.987 ($P=0.0104$)	
$F_{\mathrm{AT\times IC\times CN}}$		2.171 ($P=0.012$)		$F_{\mathrm{AP\times IC\times CN}}$		2.011 ($P=0.0100$)	
$F_{\mathrm{AT\times AP\times IC\times CN}}$		0.413 ($P=0.0399$)					

**RMSE* root mean square error, *AT* amendment type, *IC* initial concentration, *AP* amendment %, *CN* desorption cycle number. *F* values determined using SPSS software through univariate two-way ANOVA. *P* values denote degree of significance. All treatments significantly differed at $P<0.05$, when post hoc test performed with Tukey's HSD

adsorption ratios $(1/n_{\mathrm{des}})/(1/n_{\mathrm{ads}})$ denotes the hysteresis (H) constant. The value of $H<1$ denotes positive hysteresis that indicates the rate of adsorption is higher than the rate of desorption, whereas $H>1$ depicts negative hysteresis, which refers to a rate of adsorption that is less than the rate of desorption (Kumar & Singh, 2020). The H values were less than 1 for both amendments, suggesting positive hysteresis. Furthermore, H values were higher at lower pesticide concentrations than higher concentrations due to greater nonlinearity in the desorption isotherm. Both adsorption and desorption Freundlich constants are well correlated with amendment contents in the soil (Table 5). There are several factors responsible for the sorption of atrazine in FYM and VC amended soil. Few of them are hydrogen bonding, ionic bonds, charge transfer, hydrophobic interactions, cation exchanges, and physical diffusion between atrazine and soil/FYM/VC particles (Prata et al., 2003). The difference between adsorption and desorption due to which hysteresis occurs may be due to the binding of atrazine to organic matter, mainly humic acids and mineral particles present in soil (Boivin et al., 2005; Fruhstorfer et al., 1993). The carboxylic groups present in soil/soil + amendment cause hydrogen bonding between soil/soil + amendment and atrazine. As hydrogen bonds are difficult to break, there was lower

Table 5 Correlation coefficient between the Freundlich constant (K_F) for atrazine adsorption/desorption with the amendment content in soil

	Amendment		Equation	r^2_{adj}
Adsorption	FYM		$K_F=0.7146e^{0.4079(\%\mathrm{FYM})}$	0.992
	VC		$K_F=0.731(\%\mathrm{VC})+0.5202$	0.999
Desorption	FYM	LC	$K_F=0.6811e^{0.4663(\%\mathrm{FYM})}$	0.987
		HC	$K_F=4.1009e^{0.1566(\%\mathrm{FYM})}$	0.983
	VC	LC	$K_F=0.34(\%\mathrm{VC})+0.8193$	0.982
		HC	$K_F=5.153e^{0.102(\%\mathrm{VC})}$	0.998

LC lower concentration, *HC* higher concentration desorption in samples containing higher amendments (Lima et al., 2010).

The nature of reaction that occurred during the adsorption and desorption process through addition of amendments was determined through Gibb's free energy change using Eq. 8.

$$\Delta \mathrm{G} = -\mathrm{RTln}K_F \quad (8)$$

where K_F represents the Freundlich constant and R is the universal gas constant (8.314×10^{-3} kJK^{-1} mol^{-1}) and T represents the absolute temperature in Kelvin (K). All the values of ΔG were negative for both adsorption and desorption, indicating that the reaction was exothermic and spontaneous in nature (Krasucka et al., 2022). In adsorption, with increasing the amendment concentration ΔG values increase that conclude that with the increasing amendment ease of adsorption increases (Table 3). Similar results, with some exceptions, are found for desorption reactions (Table 4). ΔG value for all treatment combinations was in the range of physical adsorption (Abechi, 2018).

Conclusion

This study revealed the effects of farm yard manure (FYM) and vermicompost (VC) on the adsorption–desorption behavior of atrazine. Both amendments increased the adsorption of atrazine but the effect varied with dose and type. According to our results, FYM and VC amended soils had better adsorption for the atrazine. However, the VC had the highest adsorption for the atrazine due to the higher carbon content, aromatic, and carboxyl units when compared with FYM. Our modeling demonstrated that the PSO model best fits the kinetics results in the recommended FYM and VC doses. Among all three tested adsorption isotherms, the Freundlich adsorption isotherm model was best fitted for all treatments. The ΔG values suggested that adsorption was spontaneous and exothermic in nature. The knowledge generated from this study are very crucial for determining the fate of atrazine because it has been a problematic herbicide in tropical and sub-tropical regions due to its long persistence in groundwater. Therefore, a pre-sowing application of FYM and VC could be a promising strategy to minimize the residual toxicity of atrazine in ago-ecosystems in tropical and sub-tropical regions. However, in-depth field studies are still needed to determine the long-term effects of FYM and VC on the fate of the atrazine.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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