

Removal of Atrazine, Metribuzin, Metolachlor and Alachlor by Granular Carbon

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Abstract

Adsorption-desorption of atrazine, metribuzin, alachlor and metolachlor on granular carbon were studied in a batch study. All herbicides were highly sorbed on the granular carbon (93.8-100%). Adsorption data were subjected to the Langmuir and the Freundlich adsorption isotherms, and fitted well to the Freundlich adsorption isotherm ($r^2 > 0.96$). Except alachlor, where the isotherm was nearly linear, $1/n$ values for atrazine, metribuzin and metolachlor isotherms were < 1 , suggesting a decrease in herbicide adsorption with increasing concentration in the aqueous phase. The Freundlich adsorption parameter $[K_f(1/n)]$ values were 6813.6, 2981.8, 1420.7 and 5661.4 for atrazine, metribuzin, metolachlor and alachlor, respectively. Thus, granular carbon showed the highest adsorption capacity for atrazine followed by alachlor, metribuzin and metolachlor. However, a desorption study suggests that, except alachlor ($< 3\%$), none of the herbicides were desorbed during three desorption cycles.

Although alachlor adsorption coefficients were higher than those of metribuzin and metolachlor, it was desorbed. The Freundlich constant K_f showed a positive correlation with solubility (S) while no correlation was observed with the octanol-water partition coefficient (K_{ow}). Results of three sequential adsorption studies suggest that the order of herbicide adsorption was: atrazine $>$ metribuzin $>$ metolachlor $>$ alachlor. This is in agreement with the desorption results, which suggested that granular carbon had poor retention capacity for alachlor. Among the herbicides used in this study, granular carbon has maximum retention capacity for atrazine.

Keywords: Adsorption-desorption; Granular carbon; Atrazine; Metribuzin; Metolachlor; Alachlor.

Introduction

The success of the Green Revolution was fuelled by the extensive use of chemical fertilizers and pesticides together with high yielding varieties of crops, so as to control various pests causing damages to crop plants. This resulted in the manifold increase of these chemicals. After application to the field, part of these chemicals is used by the crops and the remaining amount either persists in the environment or is lost by various biological and/or chemical mechanisms. In many countries, the use of herbicides is more than other classes of pesticides. Due to various reasons (high water solubility, soil adsorption coefficient, longer field half-life and substantial amount of use) residues of herbicides have often been detected in water.

Atrazine, a chlorinated herbicide of the s-triazine class, is one of the most widely used pesticides in the world. Because of its extensive use, long half-life in soil (13-261 days) and water (> 200 days), and various toxic properties like endocrine disruption and change in blood hormone level, it has very high environmental significance. The atrazine residue level in the well water near the mixing and loading sites in US ranged from 0.024 to 22 mg L^{-1} [1] whereas EPA permissible limit of atrazine is $3 \text{ } \mu\text{g L}^{-1}$ in drinking water. Cohen [2] reported that due to non-point sources, concentrations of atrazine in water bodies are generally in ppb levels. Triplett et al. [3] reported the highest atrazine concentration of $0.48 \text{ } \mu\text{g L}^{-1}$ in the runoff from Ohio River watershed soon after its application, whereas in Lake Erie and River Sundusky atrazine concentrations of 0.5 - 3.5 and 5.92 - $11.3 \text{ } \mu\text{g L}^{-1}$ were observed respectively [4]. Many researchers have detected atrazine concentration up to $100 \text{ } \mu\text{g L}^{-1}$ in surface and subsurface waters [5-6]. Although atrazine concentrations are usually in the $\mu\text{g L}^{-1}$ (ppb) range, it is one of the most often water contaminants.

Metribuzin is also a triazine herbicide widely used for the control of grasses and broadleaved weeds in soybean, sugarcane and numerous

other crops. Like other triazine and triazinone herbicides, metribuzin is prone to runoff into surface waters due to its high solubility in water (1200 mg L^{-1}). Contamination of surface waters by metribuzin could result from accidental discharge or direct application to watercourses, spray and vapour drift, precipitation, or surface runoff and groundwater intrusions from treated lands. Losses primarily occur through movement in the water phase, through soil runoff as opposed to translocation with eroded soil sediment [7]. Concentrations of metribuzin detected in Canadian freshwater ranged from $0.001 \text{ } \mu\text{g L}^{-1}$ in Ontario [8], to $187 \text{ } \mu\text{g L}^{-1}$ in New Brunswick [9].

Metolachlor is a pre-emergent chloroacetamide herbicide used to control annual broadleaf weeds and grasses in corn, soybean and other crops. It inhibits cell growth and prevents the synthesis of long-chain fatty acids. It has a very high potential to contaminate ground water since it is very mobile and persistent in soil. Of the acetanilide herbicides, metolachlor appears to be the most persistent ($t^{1/2} > 200$ d in highly acidic water, 97 d in highly alkaline waters) and has the potential to leach to ground water because of its relatively high water solubility (530 mg L^{-1} at 20°C). A study [10] conducted by the Environmental Protection Agency on surface and ground water in the United States found metolachlor in 2091 of 4161 surface water samples, and in 13 of 596 groundwater samples. They reported the

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Received July 12, 2013; Accepted September 28, 2013; Published September 30, 2013

Citation: Kumar YB, Singh N, Singh SB (2013) Removal of Atrazine, Metribuzin, Metolachlor and Alachlor by Granular Carbon. J Environ Anal Toxicol 3: 196. doi: 10.4172/2161-0525.1000196

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maximum concentration of metolachlor as $12 \mu\text{g L}^{-1}$ in surface water and $0.25 \mu\text{g L}^{-1}$ in groundwater. In another study of surface water samples, metolachlor was detected in 1644 samples from 312 locations in 14 states, at a maximum concentration of $138 \mu\text{g L}^{-1}$ against the permissible limit of $100 \mu\text{g L}^{-1}$.

Alachlor, another chloroacetamide herbicide, is used as pre- or early post-emergence control of annual grasses and many broadleaved weeds mainly in maize, and also in cotton, *Brassicacae*, oilseed rape, peanuts, radish, soybean and sugarcane. Log Koc values for alachlor are in the range of 2.08-2.28, indicating that alachlor have a high to medium mobility in soil. A review on monitoring data showed that alachlor was present in ground waters in USA at levels ranging from less than 0.1 to $16.6 \mu\text{g L}^{-1}$ [11] against the permissible limit of $2 \mu\text{g L}^{-1}$.

Although a number of treatment processes are available for removal of pesticides [12-27], the problem of pesticide contamination of surface and ground water bodies still often persists as a result of non-point sources, mainly from agricultural runoff. Apart from other remediation techniques, granular carbon is the most frequently used form of carbon used for purification of water in various household and commercial water purification equipments and reverse osmosis systems. Carbon is an excellent material for the adsorption of coloured impurities, foul smells and other water contaminants. Reverse osmosis (RO) systems with carbon filtration are generally recommended for households to purify drinking water. Most of the companies claim that carbon can remove all pesticides from water while few are indicating that it cannot remove all types of contaminants. Moreover, such systems use a lot of water by continuously passing it through the system, where some adsorbed amounts may also get desorbed depends upon the chemical properties of the contaminants. Unfortunately, there is no systematic study on adsorption-desorption of individual pesticides or their mixtures on granular carbon. Keeping these points in mind, a study was carried out on the adsorption-desorption of atrazine, metribuzin, metolachlor and alachlor on granular carbon.

Materials and Methods

Materials

Granular carbon meant for using in household water filtration systems was purchased from the market. It was sieved through a 0.6 mm sieve followed by 2 mm and the 0.6-2 mm fraction was used for the adsorption-desorption studies without any further conditioning treatment. Moisture content of the granular carbon was calculated by heating 1g of carbon in an oven at 120°C till no further reduction was observed in weight. pH of the carbon was measured at 1:400 (w/v) with distilled water. Surface area of carbon was measured by Brunauer, Emmett and Teller (BET) method. Physicochemical characteristics of the granular carbon used in the study are given in Table 1. Analytical grade herbicides were procured from different pesticide companies based in India: metribuzin (95% purity) was obtained from the Bayer (India) Ltd., Mumbai, atrazine (98.8%) was obtained from Rallis India Ltd., Bangalore, and metolachlor (93.8%) and alachlor (92.3%) from Hindustan Ciba-Geigy, Mumbai. Physicochemical characteristics of the pesticides used in the study are given in Table 2.

All the solvents used were of AR grade and distilled before use. Water was refluxed with KMnO_4 followed by glass distillation. Anhydrous sodium sulfate was washed with acetone, dried in a Muffle furnace at 450°C , cooled in a desiccator and stored. Sodium chloride was washed with acetone, and dried in an oven at 200°C before use and stored.

Particle size (mm)	0.6 – 2.0
Surface area ($\text{m}^2 \text{g}^{-1}$)	561.2
Moisture content (%)	11.0
pH	6.85

Table 1: Physicochemical characteristics of granular carbon used in the study.

	Aqueous solubility (g/L)	Log Kow
Atrazine	0.03	2.75
Metribuzin	1.2	1.70
Metolachlor	0.53	3.45
Alachlor	0.14	2.63

Table 2: Relevant physicochemical characteristics of the herbicides used in the study.

Adsorption-desorption experiment

The adsorption experiment was conducted using the batch method at 1:400 (w/v) granular carbon:water ratio. Granular carbon (250 mg, oven dry basis) was taken in 250 mL conical flasks and 100 mL of aqueous solution of the desired herbicide was added. The content in conical flasks were then shaken for 24 h (sufficient time to attain the equilibrium) on a mechanical shaker. After equilibration the suspension was centrifuged at 10,000 rpm for 10 min and herbicide residues were quantified in the supernatant. The adsorption studies were carried out in triplicate at initial concentrations of 1, 2.5, 5, 7.5 and $10 \mu\text{g mL}^{-1}$ for each individual herbicide. The amount of herbicide adsorbed on granular carbon was calculated from the difference between initial and equilibrium concentration in solution after adsorption following the equation:

$$q_e = (C_0 - C) \times V / M$$

Where, q_e is the concentration of herbicide sorbed ($\mu\text{g g}^{-1}$), C_0 is the initial concentration of herbicide in solution ($\mu\text{g mL}^{-1}$), C is the equilibrium solution concentration of the herbicide ($\mu\text{g mL}^{-1}$), V is the volume of solution (mL) and M is the mass of the granular carbon (mg).

Desorption of herbicides from the granular carbon was studied in the same flasks after adsorption. After adsorption the supernatant was decanted and was replaced with the equal volume of distilled water and suspension was equilibrated for another 24 h. The suspension was centrifuged and the concentration of each herbicide was estimated in the supernatant. Total of three desorption cycles were performed for each sample. Total amount of herbicide desorbed was estimated by summing the amounts of herbicide desorbed during each desorption.

To study the cumulative adsorption capability of granular carbon for individual herbicide sequential adsorption studies were performed. After adsorption of herbicides (as mentioned above), the supernatant water was replaced with equal volume of fresh aqueous solution of same herbicide and equilibrated again for 24 h for the second adsorption. Similarly third adsorption was also performed. All the supernatant solutions were processed separately.

Extraction

Supernatant from the adsorption-desorption studies were transferred to a 250 mL separating funnel and 5 g of NaCl was added. The solution was extracted with organic solvent [ethyl acetate (atrazine and metribuzin), hexane (metolachlor) and dichloromethane (alachlor)] thrice (60+50+40 mL). Organic phase was collected, pooled and dried over anhydrous Na_2SO_4 (10 g) to remove the traces of moisture. The organic phase was concentrated to dryness on a rotary vacuum evaporator and the residues were dissolved in hexane or hexane-acetone mixture (4:1) for analysis by gas chromatography (GC).

GC analysis

Analysis of herbicides was done by gas chromatography as follows. Shimadzu gas chromatograph, model GC-17A, equipped with a ⁶³Ni electron capture detector (ECD) and fitted with HP-5 megabore column [25 m (l) × 0.53 mm (i.d.) × 2.53 μm film thickness] was used with nitrogen as carrier gas at a flow rate of 3 mL min⁻¹. The injector and detector temperatures were maintained at 240 and 330°C respectively. The oven temperatures maintained were 180°C for atrazine and metolachlor and 190°C for metribuzin and alachlor. The retention times (Rts) of atrazine, metribuzin, metolachlor and alachlor using isothermal conditions were 2.6, 3.4, 4.7 and 3.8 min, respectively.

Recovery of each herbicide from water was standardized at four fortification levels i.e. 0.001, 0.1, 1, 10 μg mL⁻¹. Recovery was more than 90% for triazine herbicides (atrazine and metribuzin), 91.3-96% for metolachlor and 92.2-94.2% for alachlor at different level of fortification.

Adsorption isotherm models

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration (q_m) against liquid phase concentration (C) graphically it is possible to depict the equilibrium adsorption isotherm. Two parameter isotherms (the Langmuir and the Freundlich) were used to explain the herbicide adsorption on granular carbon.

Langmuir model

The Langmuir [28] equation is valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Sorption is assumed to take place at specific homogeneous sites within the adsorbent. Once a molecule occupies a site, no further adsorption can take place at that site. It is given by the following equation:

$$q_e = q_m \frac{bC}{1+bC}$$

The linear form of Langmuir equation is as follows:

$$1/q_e = 1/q_m + 1/b q_m C$$

where, q_m and b, are the Langmuir constants. q_m (μg g⁻¹) represents the maximum amount adsorbed per unit mass of sorbent corresponding to complete coverage of the adsorptive sites while b (L mg⁻¹) is the Langmuir constant related to the energy of adsorption. The Langmuir constants were obtained from the plot of 1/q_e versus 1/C.

Freundlich model

The empirical Freundlich [29] equation is based on sorption onto heterogeneous surface and therefore, assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. It is given by the following equation:

$$q_e = K_f C^{1/n}$$

The linear form of Freundlich equation is presented below: log q_e = log K_f + 1/n log C

where, K_f and 1/n are the constants. The Freundlich constant K_f represents the amount of contaminant adsorbed at an equilibrium concentration of 1 μg mL⁻¹. The constant 1/n (slope) is the measure of the intensity of sorption and reflects the degree to which sorption is the function of contaminant concentration. The Freundlich constants were obtained from the plot of log q_e versus log C.

Results and Discussion

The adsorption data of atrazine, metribuzin, metolachlor and alachlor on granular carbon is presented in Table 3. Results suggest that atrazine was the highest adsorbed compound showing 98.4-100% adsorption followed by metribuzin, metolachlor and alachlor.

The herbicides adsorption data was analyzed using Langmuir equation and q_m and b parameters are given in Table 3. It is observed that monolayer capacity (q_m) of the granular carbon for herbicides (μg g⁻¹) increased in the order: metribuzin < metolachlor < atrazine < alachlor, indicating that the granular carbon has maximum capacity to adsorb alachlor (20 mg g⁻¹) followed by atrazine (5 mg g⁻¹), metolachlor (3.3 mg g⁻¹) and metribuzin (2.5 mg g⁻¹). The Langmuir model predictions are not in agreement with the actual experimental results, which showed maximum adsorption of atrazine on granular carbon while alachlor was less sorbed. Therefore, it appears that herbicide adsorption on granular carbon is not a monolayer adsorption and Langmuir equation is not suited to explain the results.

Further, adsorption data was fitted to the Freundlich equation and the parameters and the isotherm are represented in Table 3 and Figure 1, respectively. The values of correlation coefficients for all the cases were very high (R² > 0.96), indicating that the Freundlich adsorption equation satisfactorily explained the results of herbicide sorption by the granular carbon.

The Freundlich 1/n values take into account the nonlinearity in the adsorption isotherms and are the index of the intensity of adsorption. The slope (1/n) values of atrazine metribuzin and metolachlor adsorption isotherm in granular carbon were less than the unity suggesting L-type isotherms [30]. L-Type isotherms are characterized by the decrease in the adsorption at higher aqueous concentration of the compound. This indicated greater competition for adsorption sites which become limited as solute concentration in solution increased. The adsorption isotherm for alachlor appeared to be linear as 1/n value was near unity.

To compare adsorption of different herbicides in granular carbon, the 1/n (slope) values should be statistically equivalent; otherwise the comparison would be meaningless. Thus, to have a meaningful comparison K_f(1/n), product of Freundlich adsorption constant (K_f) and slope (1/n), was chosen as the parameter for comparison. The K_f(1/n) values for atrazine, metribuzin, metolachlor and alachlor were 6813.6, 2981.8, 1420.7 and 5661.4, respectively. This model suggests that the order of herbicide adsorption in granular carbon was atrazine > alachlor > metribuzin > metolachlor, in agreement with the experimental observations.

Herbicide	Langmuir			Freundlich			% Adsorption	ΔG ^a
	q _m	b	R ²	K _f	1/n	R ²		
Atrazine	5000	20	0.997	11954	0.57	0.980	98.4-100	-5.59
Metribuzin	2500	20	0.984	5626.0	0.53	0.978	95.3-99.2	-5.27
Metolachlor	3333	300	0.906	3946.4	0.36	0.961	94.2-100	-5.07
Alachlor	20000	0.5	0.998	5959.4	0.95	0.999	93.8-94.2	-5.18

^aKcal mol⁻¹

Table 3: Freundlich and Langmuir adsorption-desorption parameters for herbicide adsorption on granular carbon.

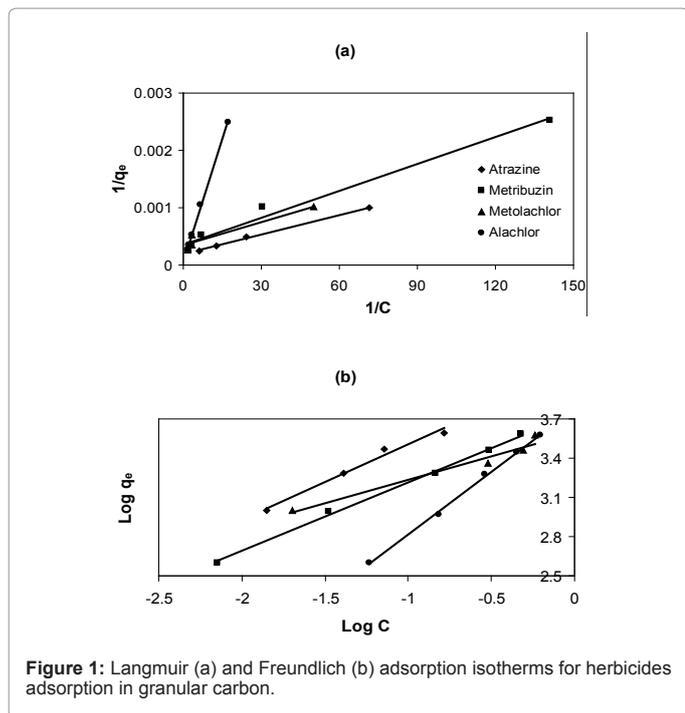


Figure 1: Langmuir (a) and Freundlich (b) adsorption isotherms for herbicides adsorption in granular carbon.

Generally, the sorption of organic compounds is correlated with their aqueous solubilities (S) and octanol-water partition (K_{ow}) coefficients [31]. The K_{ow} partition coefficients did not show any correlation with the adsorption coefficients. Among the four herbicides selected in the study, atrazine has lowest aqueous solubility (0.03 mg L^{-1}) and showed highest adsorption coefficient value. Metribuzin has highest aqueous solubility (1.05 mg L^{-1}) but it was metolachlor that showed minimum adsorption. The linear regression of $\text{Log } K_f$ and $\text{log } S$ yielded the relationship: $\text{Log } K_f = 4.0872 - 0.1447 \text{ log } S$ ($r^2 = 0.845$)

The free energy (G) values for herbicide sorption in the granular carbon were calculated using the distribution coefficient, K_d (K_d values were calculated by the linear fit of the adsorption points by plotting equilibrium concentration C ($\mu\text{g mL}^{-1}$) on x-axis and amount adsorbed qm ($\mu\text{g g}^{-1}$) on y-axis) values and the following equation: $\Delta G^0 = -RT \ln K_d$

Where ΔG is the free energy change (Kcal mol^{-1}), R is the gas constant ($1.986 \text{ cal K}^{-1} \text{ mol}^{-1}$), and T is absolute temperature. The ΔG is used as a measure of the extent of the driving force in the adsorption process. The greater the absolute magnitude of ΔG , the greater is the extent to which the adsorption reaction may take place. The ΔG values varied between -5.07 (metolachlor) and $-5.59 \text{ Kcal mol}^{-1}$ (atrazine), suggesting that the process is exothermic and spontaneous and within the range for physical adsorption, providing evidence that sorption of herbicides on granular carbon through physical processes. Highest ΔG values for atrazine suggested that atrazine was more spontaneously sorbed than the metribuzin, alachlor and metolachlor.

Results of the desorption study showed that no atrazine, metribuzin and metolachlor desorption was observed suggesting that these herbicides were strongly adsorbed by the granular carbon. Alachlor was the only herbicide that was desorbed, however at the lowest concentration of $1 \mu\text{g mL}^{-1}$ no alachlor desorption was observed (Table 4). Nearly 2-3% of sorbed alachlor was desorbed during three desorption cycles. Result of adsorption-desorption study suggested

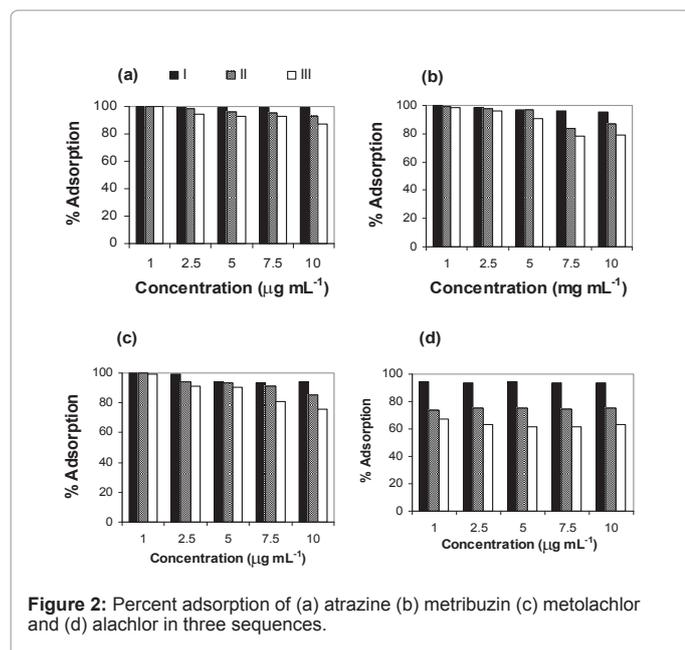
that the granular carbon has very high adsorption capacity for the selected herbicides. Except alachlor, adsorption of herbicides was concentration dependent and adsorption efficiency was better at low herbicide concentrations. Although adsorption coefficient values for metolachlor were the lowest, but, it was strongly adsorbed and was not desorbed even after three desorption cycles. On the contrary alachlor, whose adsorption coefficient was higher than the metolachlor, showed 2-3% desorption.

Sequential adsorption of all the four herbicides was studied to know the total amount of herbicide adsorbed after three adsorption cycles (Figure 2). Results suggested that percent amount of herbicide adsorbed by the granular carbon decreased after each cycle and percent decrease varied with nature of herbicide and initial herbicide concentration. During third cycle granular carbon showed maximum adsorption of atrazine (99.9-87.3%) followed by metribuzin (98.5-79.4%), metolachlor (99.1-75.8%) and alachlor (67.3-63.5%). Thus, after repeated adsorption maximum decrease in adsorption efficiency was observed for alachlor while atrazine showed minimum decrease. This might be the reason that only alachlor was desorbed during desorption experiment. Probably, compared to other three herbicides, alachlor was weakly bound at the adsorption sites, therefore was easily desorbed. That is why, in spite of the fact that alachlor had K_f higher than the metolachlor, it showed marginal desorption while no metolachlor desorption was observed. Adsorption results discussed above suggested that herbicide sorption by granular carbon was concentration dependent; therefore maximum decrease in adsorption during second and third cycle was observed at highest herbicide concentration ($10 \mu\text{g mL}^{-1}$). However, alachlor adsorption showed less concentration dependence and was in agreement with the adsorption results as alachlor adsorption isotherm was nearly C-type. After three cumulative adsorption cycle at $10 \mu\text{g mL}^{-1}$ initial herbicide concentration the amounts of atrazine, metribuzin, metolachlor and alachlor were 11.18, 10.46, 10.21 and 9.29 mg g^{-1} , respectively. These results further confirmed that the granular carbon exhibited maximum adsorption capacity for atrazine and alachlor was the least sorbed.

Granular carbon is known for its pesticide adsorption capacity; however, a comparative adsorption analysis of different herbicides is not available. Chingombe et al. [32] studied atrazine adsorption on activated carbon and reported that atrazine adsorption was concentration dependent and K_f was $139.9 \text{ mmol}^{1-1/n} \text{ m}^3 \text{ kg}^{-1}$. Results of the present study suggest that among the four herbicides used in the study, granular carbon had highest adsorption capacity for atrazine followed by metribuzin, metolachlor and alachlor. Herbicides adsorption was explained by the Freundlich adsorption isotherms.

Concentration ($\mu\text{g mL}^{-1}$)	Amount sorbed ($\mu\text{g g}^{-1}$)	Amount desorbed ($\mu\text{g g}^{-1}$) \pm SE				% Desorption
		I	II	III	Total	
1.0	384.8	0	0	0	0	0
2.5	964.4	16 \pm 0.98	6.4 \pm 0.26	0	22.4	2.32
5.0	1924	30 \pm 1.37	14.8 \pm 0.72	10.4 \pm 0.83	54.4	2.82
7.5	2890	46.4 \pm 5.33	20 \pm 2.14	14.8 \pm 0.8	81.2	2.80
10	3813.2	66 \pm 6.33	27.6 \pm 2.51	18.8 \pm 2.59	112.4	2.94

Table 4: Alachlor desorption from granular carbon into water.



Acknowledgement

Yengkhom B. Kumar is grateful to the Indian Agricultural Research Institute, New Delhi for the financial assistance.

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