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Removal of herbicides mixture of atrazine, metribuzin, metolachlor and alachlor from water using granular carbon

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Removal of atrazine, metribuzin, metolachlor and alachlor in mixture at 5 μg mL^{-1} fortification level on granular carbon has been studied using batch method. Metribuzin is found to be the most adsorbed herbicide and adsorption followed the order: metribuzin> atrazine> alachlor> metolachlor. Desorption results suggest that atrazine and metribuzin are bound irreversibly while metolachlor and alachlor are desorbed and percent desorption of alachlor (1.28%) is more than metolachlor (1.14%). Column studies using granular carbon have been carried out at fortification level of 5, 1 and 0.1 μg mL^{-1}. At higher concentration (1 and 5 μg mL^{-1}), metolachlor is least sorbed and sorption followed order: metolachlor>alachlor> atrazine>metribuzin but, at lower concentration (0.1 μg mL^{-1}), alachlor is the least adsorbed herbicide. The performance of horizontal column is found better than the vertical column.

Keywords: Granular carbon, Atrazine, Metribuzin, Metolachlor, Alachlor, Column, Removal

Safe and clean drinking water is a requirement of every living organism including human being. Due to the ever increasing population, there is always a pressure of increasing food grain production. In the race of hungry mouths and decreasing land, high yielding varieties and use of chemical fertilizers and pesticide have become unavoidable inputs which in long run have resulted in various type of contamination in environment. Water contamination is also one of them. Long (1987) reported, the contamination of groundwater by atrazine upto 22 mg L^{-1} whereas permissible limit of atrazine is 3 ppb in drinking water[1]. Pesticide residues due to runoff into surface water and nonpoint pollution due to agricultural use in ground water are found in many countries of the world. Triplet *et al.* (1978) reported the highest atrazine concentration of 0.48 ppm in the runoff from Ohio River watershed soon after its application[2]. There are also reports of atrazine detection up to 100 μg L^{-1} in surface and subsurface waters[3]. Although India is using a meager share of world pesticide consumption, but the incidence of pesticides in bottled water are examples of alarming situation. Drinking water is the most primary need and for that remediation technique like adsorption[4-12], chemical treatment[13-17] and biodegradation[18-20] are being used at commercial as well as domestic scales. Apart from other remediation techniques, granular carbon is the most frequently used carbon form used for purification of water in various household and commercial water purification systems. Carbon is a known universal material for the adsorption of coloured impurities, foul smell and other contaminants from various types of matrices. Water purification systems with carbon filtration are usually recommended for community purification of drinking water. Most of the sellers claim that it removes all impurities including pesticides. However, due to continuous flow of water through such system, there is a possibility that adsorbed amount may get desorbed depending upon the structure of contaminant. Kumar *et al.* (2013) have studied the adsorption and sequential desorption of individual herbicides on granular carbon[21]. However results may not be extrapolated when these pesticides are present in mixture. Keeping that in view, adsorption–desorption studies on granular carbon for mixture of four herbicide i.e. atrazine, metribuzin, metolachlor and alachlor were conducted. To validate the adsorption-desorption experiment results of mixture and to imitate the community system of water purification where equilibrium time is not always very high and sequential desorption possibilities are more, a column study was also conducted for the removal of four herbicides using granular carbon.

Experimental Section

Materials

Analytical grade metribuzin (95% purity) was obtained from the Bayer (India) Ltd., Mumbai, India. Analytical grade atrazine (98.8%) was obtained from Rallis India Ltd., Bangalore, India. Metolachlor (93.8%) and alachlor (92.3%) were procured from Ciba-Geigy. Physico-chemical properties of herbicides are given in Table 1. Granular carbon that is used in water filtration systems was purchased locally and 0.6 - 2 mm size fraction (obtained by seiving through a 0.6 mm sieve followed by 2 mm) was used for the adsorption-desorption studies without any further conditioning or treatment. Moisture content of the granular carbon was calculated by heating 1g of carbon in oven at 120°C till no further reduction in weight was observed and was 11%. The physico-chemical properties of granular carbon included: *p*H 6.9 measured at 1:400 (w/v) carbon:water ratio, surface area 561.2 m^2 g^{-1} measured by BET method.

Adsorption desorption experiment

The adsorption-desorption experiment for herbicide mixture was conducted using 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 mixture was added. Experiment was carried out in triplicate at initial concentration of 5μg mL^{-1} for each herbicide. The content in conical flasks were shaken for 24 h (time required to attain equilibration) on a mechanical shaker. After 24 h equilibration, the suspension was centrifuged at 10,000 rpm for 10 min and herbicide residues were quantified in the supernatant. The amount of herbicide adsorbed on granular carbon was calculated from the difference between initial and final concentration in solution after adsorption following the equation: $q_e = (C_0\text{-}C) \times V/M$

where, q_e is the concentration of herbicide sorbed (μg g^{-1}), C_0 is the initial concentration of herbicide in solution (μg mL^{-1}), $\boldsymbol{C}$ is the equilibrium solution concentration of the herbicide (μg mL^{-1}), V is the volume of solution (mL) and M is the mass of the granular carbon (mg). To study the cumulative adsorption capability of granular carbon for individual herbicide, sequential adsorption studies were performed. The process was repeated again and the granular carbon was equilibrated with fresh solution of herbicide containing 5 μg mL^{-1} of each herbicide. Total of three such cycles were performed.

Table 1 — Physico-chemical characteristics of the herbicides used in the study

Herbicide	Aqueous solubility(g L^{-1})	Log K_{ow}
Atrazine	0.03	2.75
Metribuzin	1.05	1.70
Metolachlor	0.49	3.45
Alachlor	0.14	2.63

Desorption of herbicides from the granular carbon was studied in the same flasks after three adsorption cycles. After adsorption, the supernatant was removed and replaced with equal volume of distilled water and suspension was equilibrated for another 24 h. The suspension was centrifuged and concentration of each herbicide was estimated in the supernatant. A 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.

Column experiment

Keeping in view various water purifier designs of vertical and horizontal nature, the column experiment was also performed in two manners: vertical column and horizontal column. Glass column (60 cm length × 1.5 cm diameter) was packed with 5 g of granular carbon which was sandwiched between glass wool. Distilled water fortified with herbicides mixture at 0.1, 1.0 and 5.0 μg mL^{-1} was separately passed through the vertical columns and fractions of 100/200 mL were collected. A total of 1L water of 1 and 5 μg mL^{-1} concentrations were passed through the vertical column while 6L water of 0.1 μg mL^{-1} was passed. The experiment was done in duplicate with one control where only distilled water was passed. To compare the effect of column position, the glass column was held horizontally and used for studying the herbicides removal efficiency. The percolated water contained a mixture of four herbicides at a level of 1 μg mL^{-1} of each herbicide. The rate of water percolation in both the columns (vertical or horizontal) was maintained at 0.25 mL min^{-1}.

Supernatant from the adsorption-desorption studies or column fraction collected were transferred to a 250 mL separating funnel in which 5 g of NaCl was added. The solution was extracted with organic solvent [ethyl acetate: hexane 3:7] thrice (100+70+30 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 herbicide was done by gas chromatography as follows. Shimadzu gas chromatograph, model GC-17A, equipped with a ^{63}Ni 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 temperature for analysis of herbicide mixture was programmed at 5°C min^{-1} from 145 to 200°C with hold time of 5 min and all the four compounds were separated at 5.2 (atrazine), 7.7 (metribuzin), 8.1 (metolachlor) and 6.7 (alachlor) min.

Recovery studies

Recovery of herbicide mixture from water was standardized at four fortification levels i.e. 0.001, 0.1, 1, 10 µg mL^{-1}. Extraction of herbicide mixture from water was tried with two different solvents i.e., ethyl acetate alone and ethyl acetate: hexane mixture (7:3) separately for recovery of all the four herbicides from water.

Results and Discussion

Results of recovery studies of herbicide mixture from water using two different solvents are presented in Table 2. Results indicated that ethyl acetate alone was not giving good recovery (61.6-71.8%) of acetanilide herbicides (metolachlor and alachlor) at all the three fortification levels while triazines (atrazine and metribuzin) were recovered in the range of 82.6-92.1%. Recovery with ethyl acetate: hexane mixture (7:3) gave good recoveries for all the herbicides ranging between 83-90.7%. Therefore, ethyl acetate: hexane (7:3) mixture was chosen for extraction in all the experiments.

Percent removal of atrazine, metribuzin, metolachlor and alachlor in mixture from aqueous solution after three consecutive cycles is given in Fig. 1a. The result showed that except metribuzin, sorption of atrazine, metolachlor and alachlor on granular carbon decreased after each successive cycle. Metribuzin showed 100% removal from herbicides mixture in all the three cycles. Comparison of herbicide removal efficiency with granular carbon suggested that the order of herbicide adsorption was: metribuzin> atrazine> alachlor> metolachlor. Thus, granular carbon was more effective in removing triazine herbicides than acetanilide group of herbicides from their mixture in water.

Earlier, Kumar *et al.*, (2013) reported[21] the individual adsorption of atrazine, metribuzin, metolachlor and alachlor, on granular carbon where the results suggested that the order of adsorption was: atrazine> metribuzin> metolachlor> alachlor. However, when these herbicides were present in mixture, the order changed. This suggested that in

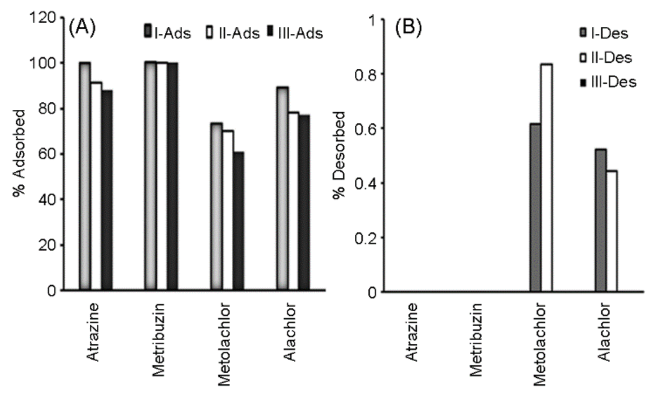

Fig. 1 — Adsorption (a) and desorption (b) of herbicide mixture on granular carbon

Table 2 — Recovery of herbicide mixture from water using different solvents

Solvent used	Fortification level (µg mL^{-1})	% Recovery* ± S.D.			
		Atrazine	Metribuzin	Metolachlor	Alachlor
Ethyl acetate	0.001	88.7±0.32	82.6±0.33	61.6±0.44	64.7±0.30
	0.1	85.8±0.51	83.5±0.49	62.7±0.69	68.7±0.69
	1.0	92.1±0.32	88.6±0.36	65.6±1.26	71.8±o.64
	10	86.3±1.04	86.2±0.40	62.4±0.74	68.6±0.45
Ethyl acetate: Hexane (7:3)	0.001	86.8±0.89	82.9±0.32	86.3±0.32	83.1±0.40
	0.1	87.0±0.49	83.1±0.85	85.3±0.44	84.8±0.2
	1.0	90.7±0.67	83.7±0.43	88.1±0.81	85±0.12
	10	89.6±0.41	82.7±0.47	87.1±0.41	83±0.88

*Average of three replicates; S.D.- Standard deviation mixture there is a competition for adsorption sites. Triazine herbicides having three nitrogen containing heterocyclic aromatic rings are more competent than the acetanilide herbicides having substituted benzene ring in structure, thus get preferably sorbed first. However, within each group the order changed when they are present in mixture. The order of herbicide sorption from mixtures cannot be explained by their octanol-water partition coefficient (K_{OW}) as metolachlor has highest K_{OW} value (3.45) while metribuzin has the lowest value (1.70). However, according to Matsui *et al*., (2002), molecules with smaller molecular weight compete better for adsorption sites[22]. Among the studied pesticides, molecular weights were in the order of metribuzin (214.3) < atrazine (215.7) < alachlor (269.8) < metolachlor (283.8).

Results of desorption studies (Fig. 1b) suggested that even after three repeated desorption cycles, both atrazine and metribuzin did not show any desorption. However, both metolachlor and alachlor, though did not desorb during third cycle, were desorbed during 1st and 2nd cycles, and the amount desorbed decreased subsequently. Comparatively, alachlor showed higher desorption (1.28% of adsorbed amount) than metolachlor (1.14% of adsorbed amount). Out of total desorbed amount, 65.38% of alachlor and 54.19% of metolachlor were desorbed in first cycle following rest in the second cycle. Thus, triazine herbicides, which were more sorbed, were retained by the granular carbon. Comparison of desorption results in mixtures during present study and individual[21] herbicides suggested that although metolachlor was not desorbed even in 10 µg mL^{-1} concentration experiments, when used alone, but in mixture desorption of metolachlor was observed even in 5 µg mL^{-1} concentration. This clearly suggested that there was competition for sorption sites when herbicides were present in mixture. Clearly, like sorption finding desorption results cannot be explained by the physico-chemical parameters of the herbicides.

Results of column studies are shown in Fig. 2. The results of vertical column study indicated that at 5 µg mL^{-1} fortification level all the four herbicides were detected in the first fraction itself, however amounts varied and were 0.001, 0.00036, 1.711 and 0.3 µg mL^{-1} for atrazine, metribuzin, metolachlor and alachlor, respectively. Concentration levels increased in last fraction and the respective values were 0.009, 0.00043, 3.884 and 0.719 µg mL^{-1}. These results suggested that at higher concentration the order of herbicide retention by granular carbon was: metribuzin> atrazine >alachlor> metolachlor.

This trend was in conformity with the result obtained in the sorption experiment. However, when leaching study was performed at 1.0 µg mL^{-1} levels, there was a change in the order of herbicide retention. At 1.0 µg mL^{-1} levels, no atrazine was recovered in the leachate even after passing 1 L solution. Concentration of metribuzin, metolachlor and alachor in first fraction were 0.00024, 0.085 and 0.10 µg mL^{-1}, respectively while respective amounts in last fraction were 0.0007, 0.38 and 0.285 µg mL^{-1}, respectively. Further decrease in herbicide initial concentration 0.1 µg mL^{-1} suggested that upto 30th fraction no atrazine, metribuzin and metolachlor were detected in the leachate. Alachlor was obtained in 22nd fraction

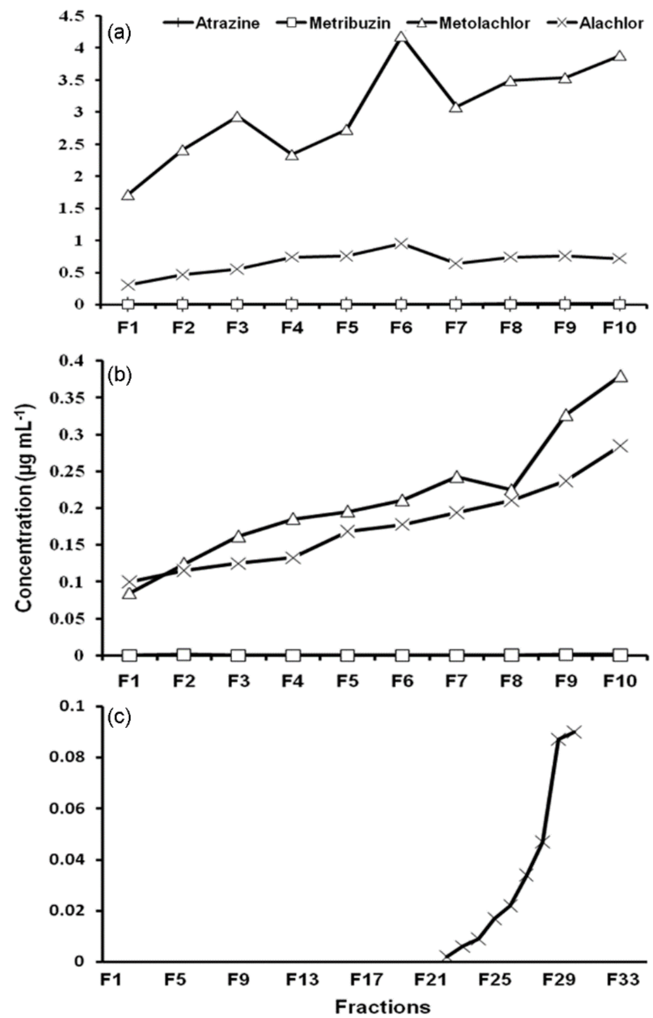

Fig. 2 — Herbicide recovery in different column fractions of granular carbon at (a) 5; (b) 1 and (c) 0.1 µg mL^{-1} level of fortification from vertical column

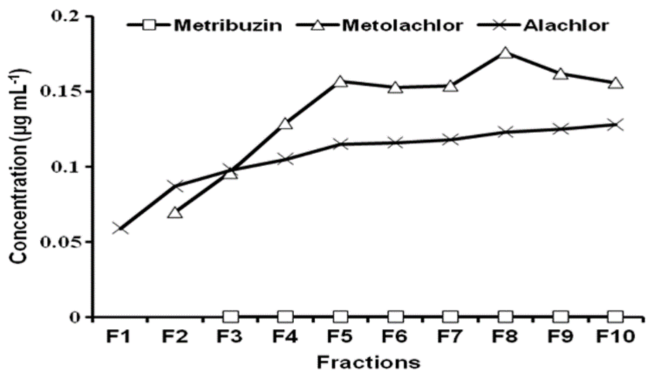

Fig. 3 — Herbicide recovery in different fractions of horizontal column of granular carbon at 1 µg mL^{-1} level of fortification

after percolating 4200 mL water. Thus, at 0.1 µg mL^{-1} concentrations, the alachlor was least retained by granular carbon while at 1.0 and 5.0 µg mL^{-1} levels, the metolachlor was the least retained herbicide. This indicated that retention of herbicides by granular carbon was dependent on the initial herbicide concentration.

Experiment of horizontal column was done in order to avoid any mass flow of water due to gravity as granular carbon column has inter-granular spaces in the packing of column. The results of horizontal column study with 1.0 µg mL^{-1} levels (Fig. 3) suggested similar trend of elution as observed with vertical column and metolachlor was the least retained herbicide. However, due to mass flow of solution greater amounts of all the four herbicides were retained in horizontal column than the vertical column. Amount of herbicides in different fractions in vertical column were nearly three times the concentration that was found in horizontal column. This may be due to a better contact of water, containing herbicide, for more time with granular carbon.

Conclusion

Granular carbon is a good material for removal of atrazine, metribuzin and metolachlor herbicides from water. Under natural conditions, where contaminated levels are in parts per million or parts per billion, granular carbon can effectively remove all the four herbicides, although alachlor is the least adsorbed herbicide. Thus, removal efficiency is affected by the herbicide concentration suggesting competitive retention. Horizontal columns were more effective than the vertical columns.

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