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Adsorption of herbicides on coal fly ash from aqueous solutions

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ABSTRACT

Development of low cost adsorbent for pesticide retention is an important area of research in environmental sciences. The present study reports the sorption potential of coal fly ash, a waste from power stations, for removal of metribuzin, metolachlor and atrazine from water. Batch sorption method was used to study the sorption of herbicides from water. The amount of herbicides sorbed increased with increase in the amount of fly ash in the suspension. The maximum capacity of the fly ash to adsorb metribuzin, metolachlor and atrazine was found to be 0.20, 0.28 and 0.38 mg/g by Freundlich equation and 0.56, 1.0 and 3.33 mg/g by Langmuir equation. Freundlich adsorption equation better explained the results of herbicides sorption in fly ash as regression coefficient (R^2) values were higher from Freundlich equation than the Langmuir equation. Adsorption isotherms were L-type suggesting that the herbicide sorption efficiency of fly ash depend on the initial concentration of herbicide in the solution and maximum removal of herbicide was observed at concentrations less than 10 μg/ml. The results of this study have implications in using the fly ash for removal of these herbicides from industrial and agricultural waste water and can find use as a material in the preparation of biobeds to minimize environmental contamination from pesticide use.

1. Introduction

Pesticides are the major input in today's intensive agriculture. Wide spread use of these agricultural inputs has caused contamination of ground and surface water resources due to their leaching and runoff losses. Improper disposal of the empty pesticide containers, washing of spray instruments and unregulated discharge from manufacturing units are other causes of water resources contamination. In past few years presence of pesticide residues in the ground water resources has grown significantly and has become an intensive and burning issue of discussion. Ground water contamination affects the health of human beings as it is being directly used for drinking purpose. Number of methods used for the cleanup of water includes: oxidation with ozone, biological method, ion exchange, electrochemical oxidation, reverse osmosis, photocatalytic degradation and adsorption. Each method has its own merits and limitations in application. Despite the availability of number of clean up methods, adsorption process still remains the best method as it is not specific to only one type of contaminant and removes most of the contaminants. Activated charcoal is the most commonly used adsorbent for removing pesticide residue from contaminated water [1–3]. However, because of high cost of activated charcoal, its use at large scale is very limited. In order to overcome this problem, exploitation of newer, cheaper and indigenous waste materials for the removal of pesticides from water and waste water have been the focus of intense research. Materials investigated as adsorbents for pesticides includes: charcoal from agro waste [4–6], straw [7,8], date and olive stones [9,10], wood chips/corn cob [8], lignocellulosic substrate from agro-industry [11], bark [12], watermelon peel [13], baggasse fly ash [14,15].

Metribuzin (4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5-one), metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylphenyl)] and atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) are commonly used herbicides with varying aqueous solubility and have been discovered in surface and ground water sources [16–18]. Metribuzin is characterized by its high water solubility (1050 mg/l) and low adsorption in soil (K_{oc} (organic carbon) = 60), therefore, has high potential for movement in the soil profile. The United States Environmental Protection Agency (US EPA) maximum advisory concentration for metribuzin in drinking water is 175 μg/l [16]. Metolachlor has been detected in surface and subsurface water and peak metolachlor concentration in subsurface drain water discharge of experimental plots ranged from 0.1 μg/l to more than 100 mg/l [19,20]. The USEPA health advisory level of metolachlor for drinking water is 10 μg/l. Like wise, atrazine is the most widely detected herbicide in the surface and ground water in the USA. Poinke et al. [21] reported that 14 of the 20 well water samples collected from Pennsylvania contained atrazine in concentrations ranging between 13 and 1110 ng/l.

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Table 1
Physico-chemical characteristics of the fly ash.

Parameter	Value
pH[a]	6.75
Organic carbon (%)	0.17
Particle size (%)	
Sand	30.2
Silt	50.0
Clay	19.8
Specific surface area ($m^2\ g^{-1}$)	285

[a] pH was measured at 1:1.25 fly ash:water ratio.

The fly ash, a by-product from lignite-fired thermal power stations is a low cost adsorbent and has shown significant adsorption capacity for organic pollutants [22]. Few reports have highlighted the pesticide sorption potential of fly ash [23,24] and have recommended it for use in the removal of pesticides from water samples [5,6] Therefore, in the present investigation I studied the sorption of metribuzin, metolachlor and atrazine from their aqueous solutions in the fly ash. The study can have implications in exploiting fly ash as a low cost adsorbent for the cleanup of waste water and cutoff barrier to retard pesticide transport.

2. Materials and methods

2.1. Sorbent

Fly ash was collected from the Indraprastha Thermal Power Station, New Delhi, India. Indian coal is mainly bituminous coal that produces nearly 45% fly ash. Fly ash produced from bituminous coal mainly contains SiO_2, Al_2O_3 and Fe_2O_3. The physico-chemical characteristics of the fly ash determined using standard analytical procedures [organic carbon (OC) content [25]; soil mechanical fractions [26], surface area [27]] are represented in Table 1.

2.2. Herbicides

Analytical grade metolachlor (97.8% purity) was purchased from the Riedel de Haen Laborchemikalien, GmbH and Co. KG, Sleez, Germany. Analytical grade metribuzin (95% purity) was obtained from the Bayer (India) Ltd., Mumbai, India. Analytical grade atrazine was obtained from Rallis India Ltd., Banglore, India. The characteristics of the herbicides are given in Table 2. The solvents used were of analytical grade and were purchased locally.

2.3. Sorption studies

Kinetics of metribuzin, metolachlor and atrazine sorption on fly ash was studied at a 1:20 fly ash to water ratio by equilibrating 0.5 g of fly ash with 10 ml aqueous solution of metribuzin, metolachlor or atrazine (10 μg/ml) for 10, 20, 30, 60, 120, 360 min and 24 h on an end over end shaker. A blank, without fly ash, was maintained to observe any sorption of herbicides on the glass surface or degradation during the equilibration. After equilibration fly ash suspension was centrifuged at 3500 rpm for 20 min and herbicide residues were quantified in the supernatant. The amount of herbicide adsorbed by the fly ash was calculated from the difference of initial and final concentration of herbicide in the supernatant. There was no sorption of herbicides on the glass surface and were stable during the equilibration period.

To study the effect of amount of fly ash on herbicides sorption, varying amounts of fly ash (0.1–2 g) were equilibrated with 10 ml aqueous solution of metribuzin, metolachlor or atrazine (10 μg/ml) for 2 h. A blank, without fly ash, was maintained as control. After equilibration fly ash suspension was centrifuges at 3500 rpm for 20 min and herbicide residues were quantified in the supernatant. The amount of herbicide adsorbed by the fly ash was calculated as mentioned above.

To obtain adsorption isotherms for metribuzin, metolachlor and atrazine fly ash (1.0 g for metribuzin or metolachlor and 0.2 g for atrazine) and 10 ml aqueous solution of herbicides in 50 ml glass test tubes were equilibrated on an end-over-end shaker for 2 h at room temperature. A blank, without fly ash, was maintained as control. The concentration of herbicides ranged between 2.5 and 500 μg/ml for metribuzin, 2.5 and 200 μg/ml for metolachlor and 2.0 and 10 μg/ml for atrazine and each concentration was replicated three times. After equilibration fly ash suspension was centrifuged at 3500 rpm for 20 min and herbicide residues were quantified in the supernatant. The amount of herbicide adsorbed by the fly ash was calculated as mentioned above.

Desorption of herbicides from fly ash was studied in the same tubes after adsorption and only two concentrations were chosen for desorption. After adsorption study 5 ml of supernatant was removed and was replaced with 5 ml of fresh distilled water and the suspension was equilibrated again for 2 h. After attaining equilibrium the fly ash suspension was centrifuged at 3500 rpm for 20 min, supernatant was decanted and the herbicide residues were quantified in the supernatant. The fly ash pellet obtained was subjected to two more desorption cycles. Total of three desorptions were performed for each sample and total amount desorbed was calculated by adding the amounts of herbicides desorbed during each desorption.

To study the effect of particle size of fly ash on adsorption of metribuzin, metolachlor and atrazine, the fly ash was segregated in to three different size fractions (>250, 150–250, <150 μm) using British standard metallic sieves. Then, sorption of all the three herbicides was studied in different sized fractions of the fly ash in the manner as mentioned above.

2.4. Extraction and analysis

The herbicide residues in water samples were extracted by shaking the samples (5 ml) with ethyl acetate (5 ml) for 1 min. After shaking, the samples were allowed to stand for 1 min and 1 g of anhydrous sodium sulfate was added to each tube to remove any trace of moisture from the ethyl acetate. Herbicide residues in the ethyl acetate were analysed by gas–liquid chromatography as described earlier [24,28]. The instrument used was a Hewlett-Packard (Palo Alto, CA) gas chromatograph, model 3840, equipped with a ^{63}Ni electron-capture detector and fitted with HP-1 column [10 m (length) × 0.50 mm (i.d.) with 2.53 μm film thickness]. The operating conditions were: column, 175 °C for metolachlor and 200 °C for metribuzin and atrazine; injector, 300 °C; detector, 300 °C; carrier gas (nitrogen) flow rate 4.5 ml/min. The recovery of all the three herbicides from water at fortification levels of 0.1–10 μg/g fly ash was more than 90%.

Table 2
Properties of the herbicides used in the study.

Herbicide	Aqueous solubility (g/l)	Log K_{ow}
Metribuzin	1.05	1.70
Metolachlor	0.49	3.45
Atrazine	0.03	2.75

3. Results and discussion

The results of kinetics of metribuzin, metolachlor and atrazine indicate that sorption of all the herbicides is very fast and more than 80% of the herbicides were sorbed on fly ash in the initial