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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

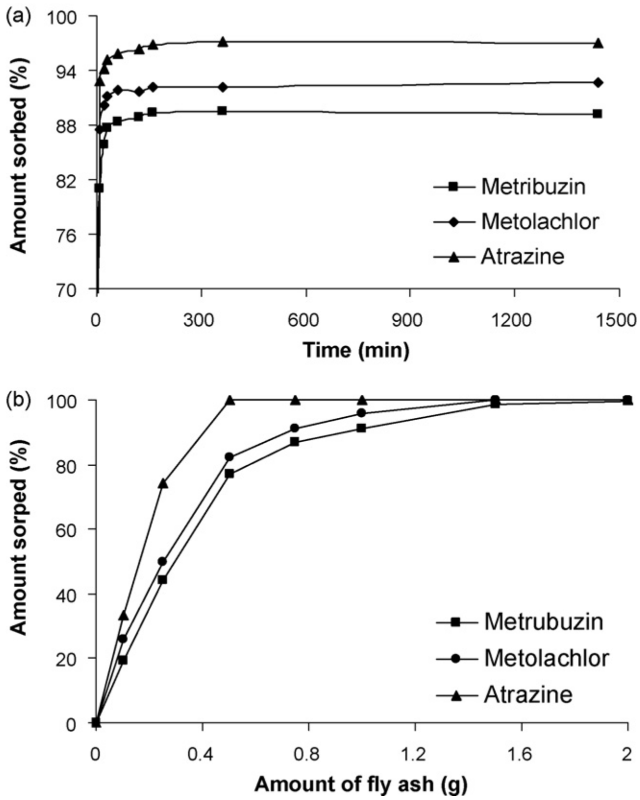


**Fig. 1.** Kinetics (a) and effect of amount of fly ash (b) on metribuzin, metolachlor and atrazine sorption. Initial concentration of herbicides used was 10 μg/ml.

10 min (Fig. 1(a)). There was no appreciable change in the sorption of the herbicides on fly ash after 120 min. Therefore, shaking of fly ash–water suspension for 2 h was chosen as the equilibration time for attaining state of equilibrium. Also, among the herbicides selected, fly ash has maximum sorption capacity for atrazine followed by the metolachlor and metribuzin, respectively.

The effect of amount of sorbent on the metribuzin, metolachlor and atrazine sorption is represented in Fig. 1(b). The results of this experiment are critical in selecting the fly ash:solution ratio for further sorption studies. The amount of herbicides sorbed in fly ash increased with increase in the amount of sorbent in the suspension. The sorption of atrazine was nearly 100% when amount of fly ash in the solution (10 ml) was 0.5 g. The amount of fly ash required for 100% sorption of metolachlor was 1.5 g per 10 ml solution. However, even at fly ash: solution (w/v) ratio of 2:10, metribuzin showed nearly 99.0% of sorption. Therefore, for rest of the studies fly ash:solution used was 1:10 for metribuzin and metolachlor, and 1:50 for the atrazine.

Adsorption data for metribuzin, metolachlor and atrazine in fly ash was fitted to the Freundlich adsorption equation:

$$\log C_{\text{ads}} = \log K_{\text{f}} + \frac{1}{n} \log C_{\text{e}}$$

where $C_{\text{ads}}$ is the amount of herbicide adsorbed at equilibrium (μg/g), $C$ is the equilibrium concentration of herbicides (μg/ml), and $K_{\text{f}}$ and $1/n$ are the constants. The Freundlich constant $K_{\text{f}}$ (intercept) represents the amount of contaminant adsorbed at an equilibrium concentration of 1 μg/ml. 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 (Fig. 2(a) and Table 3). The values of correlation coefficient for all the cases were very high ($R^2 > 0.99$), indicating that the Freundlich adsorption equation satisfactorily explained the results of herbicide sorption in fly ash and the results were significant at 99% levels. Earlier, Alam et al. [5] showed that compared to the Langmuir adsorption equation, Freundlich adsorption equation better explained the results of atrazine sorption in bottom fly ash.

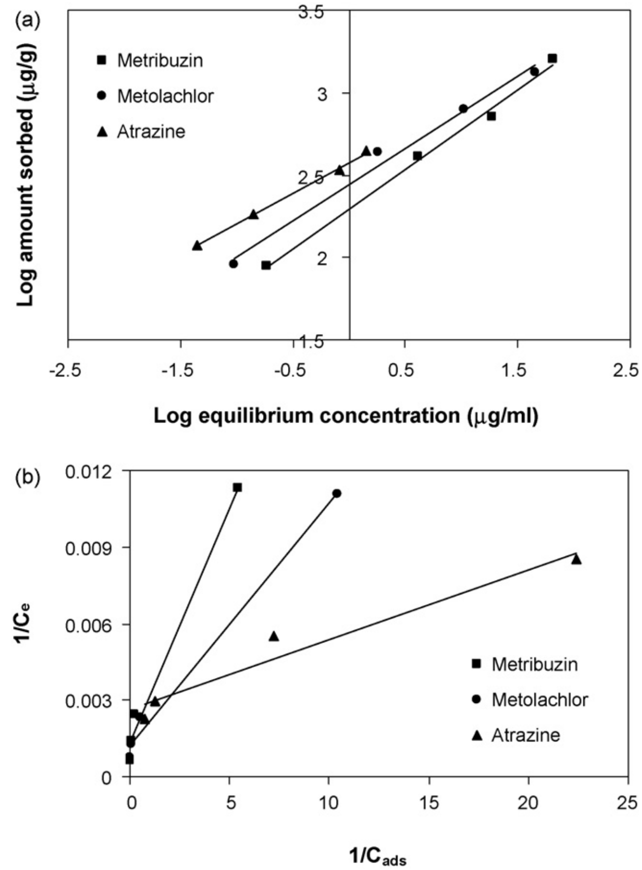


**Fig. 2.** Freundlich (a) and Langmuir (b) adsorption isotherms for metribuzin, metolachlor and atrazine in fly ash.

The slope ($1/n$) values for metribuzin, metolachlor and atrazine adsorption in fly ash were <1 suggesting nonlinear adsorption isotherms. The slope value of <1 indicated L-type isotherms, which are characterized by the decrease in the adsorption at higher aqueous concentration of compounds, thus, sorption of all the three herbicides in the fly ash was concentration dependent [29]. This type of adsorption isotherms are observed when the molecules are sorbed in a flat position, not suffering a strong competition from the water molecule, which explain the high affinity to sorbent for solute at low concentrations. However, as the concentration increases sorption sites become limiting, therefore, sorption decreases. Earlier, Konstantinou and Albanis [23] and Majumdar and Singh [24] have reported L-type adsorption isotherms for pesticide sorption in fly ash–soil mixtures.

Comparison of $K_{\text{f}}$ values for metribuzin, metolachlor and atrazine indicated that sorption capacity of fly ash for atrazine is maximum (0.38 mg/g) followed by metolachlor (0.28 mg/g) and metribuzin (0.20 mg/g). The order of herbicides sorption in fly ash

**Table 3**
Adsorption parameters for metribuzin, metolachlor and atrazine sorption in fly ash.

| Pesticide | Freundlich constants | | | Langmuir constants | | |
|---|---|---|---|---|---|---|
| | $K_{\text{f}}$ | $1/n$ | $R^2$ | $q_{\text{m}}$ | $b$ | $R^2$ |
| Metribuzin | 199.3 | 0.48 | 0.99 | 555.6 | 769.2 | 0.99 |
| Metolachlor | 277.4 | 0.44 | 0.99 | 1000.0 | 833.3 | 0.99 |
| Atrazine | 379.4 | 0.38 | 0.99 | 3333.3 | 370.4 | 0.95 |

**Table 4**
Amount of metribuzin, metolachlor and atrazine desorbed from fly ash.

| Concentration (μg/ml) | Amount sorbed (μg/g) | Amount desorbed (μg/g) | | | | % desorption |
|---|---|---|---|---|---|---|
| | | I | II | III | Total | |
| Metribuzin | | | | | | |
| 10 | 98.2 | 0.77 | 0.52 | 0.18 | 1.47 | 1.49 |
| 100 | 786 | 86.7 | 64.1 | 37.4 | 188.2 | 23.9 |
| Metolachlor | | | | | | |
| 10 | 98.9 | 0 | 0 | 0 | – | Nil |
| 100 | 896 | 35.5 | 16.0 | 7.6 | 59.1 | 6.4 |
| Atrazine | | | | | | |
| 10 | 445 | 32.5 | 4.9 | 3.0 | 40.4 | 9.07 |

can be explained by their aqueous solubility as sorption of organic compounds is generally inversely proportional to their aqueous solubilities [30]. Aqueous solubility of metribuzin, metolachlor and atrazine are 1.05, 0.49 and 0.33 g/l, respectively. Thus, atrazine, which has lowest aqueous solubility among the tested compounds, was maximum sorbed, while metribuzin having maximum aqueous solubility was the least sorbed.

Further, adsorption data was analyzed in the light of Langmuir equation:

$$\frac{1}{C_{ads}} = \frac{1}{q_m} + \frac{1}{q_m b C_e}$$

where $q_m$ is the Langmuir constant related to maximum monolayer capacity and $b$ is the Langmuir constant related to the energy of adsorption. The plot between $1/C_{ads}$ and $1/C_e$ for the adsorption of various herbicides is presented in Fig. 2(b). The values $q_m$ and $b$ have been evaluated from the intercept and slope of these plots and are given in Table 3. It is observed that monolayer capacity ($q_m$) of the fly ash for herbicides (μg/g) increased in the order: metribuzin < metolachlor < atrazine, indicating that the fly ash has maximum capacity to adsorb atrazine (3.33 mg/g) followed by metolachlor (1.00 mg/g) and metribuzin (0.56 mg/g). This is similar to the results for herbicide sorption observed by the Freundlich adsorption isotherm, however, observed values for herbicide adsorption capacity using Langmuir equation are nearly 2.5–9 times higher then the values observed using Freundlich equation. Further, parameter $b$, which is the constant for the adsorption process and reflects the affinity of the adsorbent for herbicide, indicated that the fly ash has maximum affinity for metolachlor and least for atrazine. This observation is not in line with the previous results which indicated that fly ash has highest affinity for atrazine. Also, the correlation coefficient ($R^2$) values for herbicides sorption using Langmuir isotherms ranged between 0.95 and 0.99, which are lower then the corresponding values obtained using Freundlich equation. Further, results of second experiment indicated that at a given fly ash:solution ratio fly ash has maximum retention capacity for atrazine, followed by metolachlor and metribuzin. Therefore, based on the above observations it appears that the Freundlich isotherm best explained the results of metribuzin, metolachlor and atrazine sorption in the fly ash as correlation coefficient values for herbicide sorption were highly significant (99% level) using Freundlich isotherm.

Comparison of the pesticide removal efficiency of fly ash with other low cost adsorbents used by previous workers was made. Alam et al. [5] evaluated five low cost adsorbents, viz. wood charcoal, rubber granules, bottom ash, macro-fungi *Sajor caju* and *Florida* to remove atrazine from drinking water. Wood charcoal showed the best atrazine adsorptive capacity with $Q_{max}$ of 0.80 mg/g followed by 0.47 mg/g by rubber granules. Bottom ash, *Sajor caju* and *Florida* gave poor performance. Sharma et al. [6] studied the removal of atrazine (0.05 and 0.1 mg/l levels) using wood charcoal, coconut shell charcoal, fly ash, coconut fiber charcoal, bag-

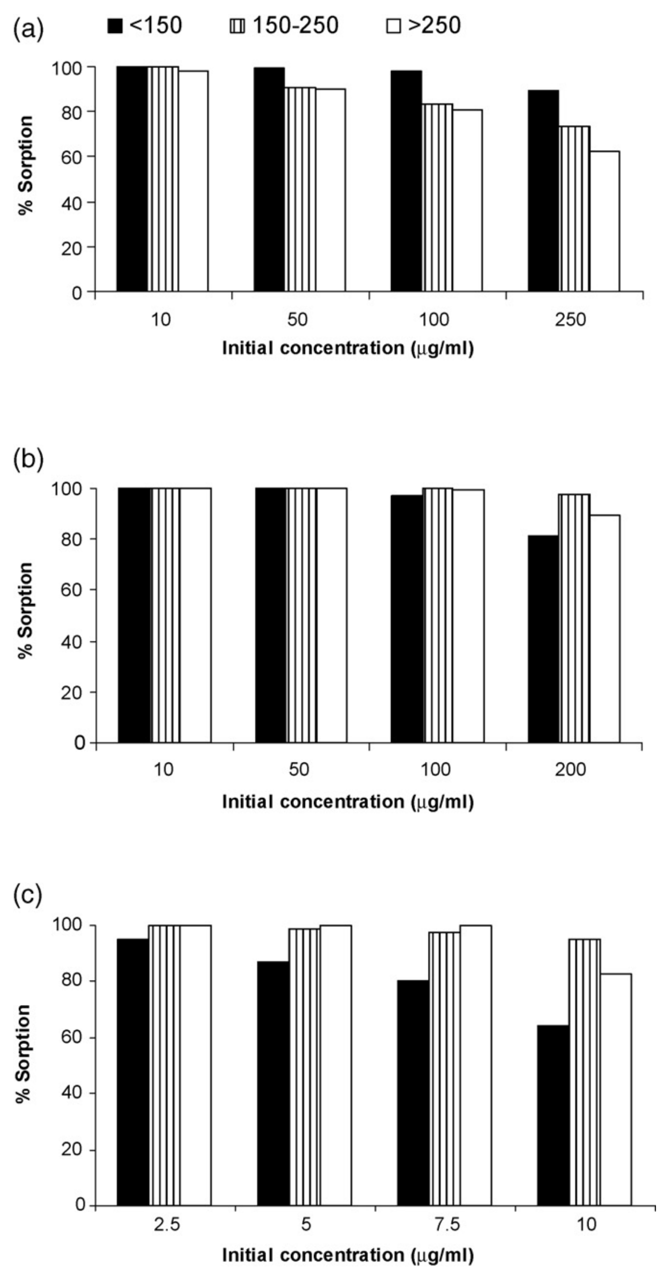


**Fig. 3.** Effect of fly ash particle size on (a) metribuzin, (b) metolachlor and (c) atrazine sorption.

gasse charcoal and saw dust. Both wood charcoal and coconut shell charcoal removed more than 90% of atrazine from water. Fly ash and coconut fiber charcoal adsorbed nearly 85% of atrazine. Baggasse charcoal and sawdust removed 75–80% atrazine. Thus, a result of present study suggests that fly ash has good capacity to remove pesticides from their aqueous solution and at low pesticide concentrations (<10 μg/ml) it can remove more then 99% of contaminant when fly ash:solution ratio used was 1:10.

Desorption of metribuzin, metolachlor and atrazine was studied in the samples after sorption at concentrations of 10 and 100 μg/ml for metribuzin and metolachlor while atrazine desorption was studied only at 10 μg/ml concentration. Results in Table 4 indicate that desorption of the sorbed compounds from fly ash was concentration dependent. Lesser amounts of herbicides were desorbed from the fly ash when sorption was carried out at low concentrations. Only 1.5% of sorbed metribuzin was released after 3 repeated desorption from fly ash when sorption was carried out at 10 μg/ml concentration. However, at 100 μg/ml concentration 24% of the sorbed metribuzin was desorbed during 3 successive desorption. No metolachlor was desorbed from the fly ash at 10 μg/ml concentration. On the other hand, at 100 μg/ml concentration 6.4% of sorbed metolachlor was desorbed. Desorption of atrazine was studied only at 10 μg/ml concentration and during 3 successive desorption nearly 9% of the sorbed atrazine was desorbed. These results suggest that if we compare desorption of metribuzin, metolachlor and atrazine from fly ash at 10 μg/ml concentration, atrazine is the maximum desorbed herbicide followed by metribuzin and metolachlor. However, it should be noticed that as fly ash: solution ratio for desorption of herbicides were different for different herbicides (1:10 for metribuzin and metolachlor and 1:50 for atrazine), therefore this comparison may not give realistic picture.

Further, the effect of particle size of fly ash on the sorption of all the three herbicides was also studied (Fig. 3). The results clearly indicate that the particle size of fly ash did affect the sorption of herbicides. At lower herbicide concentrations fly ash particle size had no effect on herbicides sorption. However, at higher concentrations effect of particle size is clearly visible, but, no definite trend was observed. At higher herbicide concentrations 150–250 μm fraction exhibited higher sorption for metolachlor and atrazine, while in case of metribuzin it was the <150 μm fraction, which showed maximum adsorption. Although surface area of different size fractions of fly ash was not measured, but, assuming that smallest size fraction (<150 μm) of fly ash will have maximum area, results obtained cannot be explained. Thus, at lower concentrations, which are generally expected in natural environment, fly ash particle sizes do not affect its herbicide sorption capacity.

## 4. Conclusion

It may be concluded from the present study that coal fly ash has significantly high retention capacity for metribuzin, metolachlor and atrazine. Freundlich adsorption isotherm appears to explain the sorption of herbicides in the fly ash. Atrazine was maximum sorbed followed by metolachlor and metribuzin. The herbicide sorption efficiency of fly ash depended on the initial concentration of herbicide in the solution and maximum removal of herbicide was observed at lower concentrations, which are generally encountered in the water samples. The study recommends that fly ash can be exploited as low cost adsorbent for chosen herbicides from waste water and run off water from agricultural soils.

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