

## Evaluation of the efficiency of fly ash from thermal power plant in controlling aquatic pollution

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**Abstract :** Contamination of ground water due to geoenvironmental causes is a worldwide problem including India. The problem further aggravates due to anthropogenic activities particularly through indiscriminate use of ground water. The geogenic route is mainly the dissolution and leaching of minerals deposits like of arsenopyrite, apatite and fluorite. This results in elevated concentration of arsenic and fluoride in drinking water and subsequent health hazards. The present report describes the use of fly ash for removal of both arsenic and fluoride in water. The operational parameters and the extent of removal are determined. The suitable condition for adsorption is evaluated from the nature of the isotherm curves and thermodynamic constants. A comparison is made with activated carbon in terms of the efficiency as well as cost of operation.

**Keywords :** Ground water, arsenic, fluoride, adsorption, fly ash.

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### Introduction

In recent years Bengal Basin is under the threat of pollution and environmental deterioration for various reasons<sup>1</sup>. In India, the extent and magnitude of fluorosis (fluoride related disease) indicated that at least 213 districts of 18 states, including four districts of West Bengal, are affected, the population at risk is estimated to be 66 million accounting roughly 9.4% of the total rural population<sup>2</sup>. The scale of arsenic problem is serious in West Bengal, India, where nine districts out of eighteen are badly affected<sup>3</sup>.

Thus to alleviate human sufferings due to of arsenic and fluoride in water some techno feasible and cost effective adsorption procedure is evaluated in the present communication. In continuation of our earlier reports on fly ash as an adsorbent, removal studies of arsenic and fluoride are carried out in the present one<sup>4</sup>. The performance efficiency of fly ash together with the feasibility of the process is evaluated in terms of experimental parameters, isotherm and thermodynamic constants. It is observed that the process is pH dependent and fly ash can be used effectively for controlling the arsenic contamination, though the capacity of fly ash is comparatively less than activated carbon. The adsorptive efficiency of fly ash can be improved by chemical modification.

### Results and discussion

In order to study the effectiveness of the fly ash as an adsorbent both the physico-chemical parameters and the surface characteristics were determined following standard procedure<sup>5</sup>. The composition of fly ash is : SiO<sub>2</sub> (72.90%), Fe<sub>2</sub>O<sub>3</sub> (3.70%), Al<sub>2</sub>O<sub>3</sub> (14.51%), CaO (2.00%), MgO (0.80%), loss on ignition (8.99%), density (3.24 g cm<sup>-3</sup>), surface area (12.97 cm<sup>2</sup>). The X-ray diffraction pattern and the scanning electron microscope image at different magnifications reveal the porous texture of fly ash. Presence of silica, alumina and iron oxides in fly ash together with high surface area and porosity makes it a good adsorbent<sup>6</sup>.

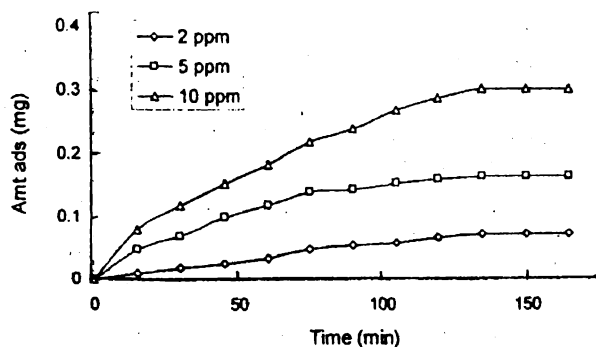
Batch experiments are carried out to investigate the sorptive characteristics of fly ash. The sensitivity of the process for the shaking, time and speed, pH, particle size, fly ash dosage, temperature and initial solute concentration are tested. Adsorption isotherms are evaluate to determine the sorptive capacity<sup>7</sup> of fly ash for the solutes. The variables for interaction of solutes with fly ash are indicated in the Table 1.

With an increase in initial solute concentration ( $C_0$ ), the amount of solute adsorption increases both for arsenic and fluoride but to different extent. The time required for attainment of equilibrium is different for ar-

**Table 1.** Range of operational variables studied for solute adsorption

Variables	Range
Initial concentration ( $\text{mg dm}^{-3}$ )	2-10
pH	1.0-10.0
Temperature (K)	303-323
Dose of FA (g)	0.5-2.0
Particle size ( $\mu\text{m}$ )	53-125
Agitation time (min)	Upto 300
Agitation speed (rpm)	100-400
Volume ( $\text{cm}^3$ )	50

senic and fluoride. For a particular solute concentration, as the dose of fly ash increases the amount of adsorption increases gradually<sup>8</sup>. Each solute adsorption on fly ash takes place at a rate proportional either to solute concentration or to the vacant sorption sites<sup>9</sup>. The dose of fly ash in  $50 \text{ cm}^3$  solution was varied from 0.5 to 2.0 g. The maximum adsorption for arsenic and fluoride is found to be 64 and 74% respectively corresponding to initial concentration of  $2 \text{ mg dm}^{-3}$  at 313 K that decreases to 55 and 61% respectively as the initial concentration increases to  $10 \text{ mg dm}^{-3}$ . With a definite initial solute concentration, the adsorption of both arsenic and fluoride decreases with increase in temperature. The variations of particle size greatly influence the adsorption of both the solutes. Higher surface area, i.e. lower particle size, favors solute adsorption due to availability of much adsorption sites for both the cases<sup>10</sup>. Adsorption is a time dependent process, becoming greater with increasing time. With progress in shaking time the solute adsorption is found to improve sharply at the initial stage. Fig. 1 represents the adsorption behavior of fluoride as a representative case. The initial enhanced adsorption rate decreases gradually as

**Fig. 1.** Influence of shaking time on adsorption of fluoride.

the equilibrium time is approached and becomes virtually constant near equilibrium<sup>11</sup>. The equilibrium adsorption time was found to be 180 min for arsenic and 135 min for fluoride. It is evident that the process is kinetically feasible as indicated by the  $t_{1/2}$  value. The  $t_{1/2}$  value is determined to be 60 and 45 min for fluoride and arsenic respectively. The increased speed of shaking improves the adsorption extent of solute for a particular set of condition<sup>8</sup>. pH of the working solution is found to have a prominent role which governs the mechanism of adsorption. The zero point charge ( $\text{pH}_{\text{zpc}}$ ) of fly ash and the specific solute species present in the solution condition determine the adsorption pattern and extent of adsorption<sup>12</sup>.

**Adsorption isotherm :** The feasibility of the process was tested from the study of the adsorption isotherm. Both the Langmuir and the Freundlich isotherms are tested to find out the best fit condition for arsenic and fluoride in solution. The main underlying assumptions for the application of the Langmuir isotherm are that all surface sites are homogeneous and it predicts the formation of monolayer of solute on the adsorbent sites<sup>13</sup>. The Freundlich isotherm, on the other hand, does not predict monolayer coverage, and the surface coverage theoretically increases without limitation with increasing solute concentration<sup>14</sup>.

Langmuir isotherm is expressed as :

$$C_e/q_e = (1/Qb) + (C_e/Q) \quad (1)$$

where,  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent at equilibrium,  $C_e$  is the equilibrium concentration of solute in solution,  $Q$ ,  $b$  are empirical constants, related to the monolayer capacity and the energy of adsorption respectively. When  $C_e/q_e$  is plotted against  $C_e$ , a straight line having a slope  $1/Q$  and an intercept  $1/Qb$  is obtained, from which  $Q$  and  $b$  are evaluated.

The Freundlich isotherm is expressed as :

$$q_e = K_f C_e^{1/n} \quad (2)$$

or in the linear form as

$$\log q_e = \log K_f + 1/n \log C_e \quad (3)$$

where  $K_f$  and  $n$  are constants characteristic of the system, indicating adsorption capacity and adsorption intensity respectively. Plot of  $\log q_e$  versus  $\log C_e$ , should yield a straight line with a slope of  $1/n$  and intercept of  $\log K_f$ . The best isotherm equation to use in the present situation

is determined by comparing the goodness of fit of the data and regression coefficient parameter ( $R^2$ ). It is found that adsorption data could satisfy either of the isotherms (Table 2).

cess occur through increased randomness.

*Cost versus efficiency of the process in comparison to activated carbon* : When activated carbon is used as an adsorbent instead of fly ash a similar trend is observed

**Table 2.** Isotherm constants with regression parameters for the solutes

Temp. (K)	Arsenic				Fluoride			
	$Q \times 10^2$ (mg g <sup>-1</sup> )	$b \times 10^2$ (dm <sup>3</sup> mg <sup>-1</sup> )	$K_f$	$1/n$	$Q \times 10^2$ (mg g <sup>-1</sup> )	$b \times 10^2$ (dm <sup>3</sup> mg <sup>-1</sup> )	$K_f$	$1/n$
	(R) <sup>2</sup>		(R) <sup>2</sup>		(R) <sup>2</sup>		(R) <sup>2</sup>	
323	56.96 (R <sup>2</sup> = 0.9532)	25.18	2.02 (R <sup>2</sup> = 1.000)	0.703	67.29 (R <sup>2</sup> = 0.8442)	29.44	1.85 (R <sup>2</sup> = 0.9060)	0.617
313	74.99 (R <sup>2</sup> = 0.9940)	12.77	2.22 (R <sup>2</sup> = 0.9991)	0.792	61.31 (R <sup>2</sup> = 0.9380)	24.30	2.02 (R <sup>2</sup> = 0.9994)	0.701
303	47.88 (R <sup>2</sup> = 0.9618)	17.60	1.99 (R <sup>2</sup> = 0.9998)	0.688	43.27 (R <sup>2</sup> = 0.9691)	28.08	1.989 (R <sup>2</sup> = 0.9929)	0.688

In order to study the feasibility of the process and application of fly ash, the thermodynamic parameters  $\Delta G$  (free energy change),  $\Delta H$  (change in heat of adsorption) and  $\Delta S$  (change in entropy) are evaluated from the following eqs. (4)–(6).

$$K_c = C_{AC}/C_e \quad (4)$$

$$\Delta G = -RT \ln K_c \quad (5)$$

$$\Delta H = \Delta G + T\Delta S \quad (6)$$

From eqs. (4)–(6), it can be written<sup>15</sup> that,

$$\ln K_c = -\Delta H/RT + \Delta S/R \quad (7)$$

A plot of  $\ln K_c$  vs  $1/T$  yield a straight line from which  $\Delta H$  and  $\Delta S$  are calculated from the slope and intercept respectively. The values of  $\Delta H$  and  $\Delta S$  are presented in Table 3. The free energy change for all the solutes are negative indicating the feasibility of the process as well as its spontaneous nature.  $\Delta H$  values are negative for both the solutes, indicating the exothermic nature. This was also indicated by the increased adsorption with lower temperature. The positive  $\Delta S$  values suggest that the pro-

cess occur through increased randomness. Taking the case of equilibrium adsorption time into consideration, it was found that for both fly ash and activated carbon equilibrium are attained within 3 h of contact period. However, though the adsorption efficiency of fly ash is less compared to activated carbon the cost of fly ash is much lower compared to even the cheapest variety of commercially available carbon. Therefore fly ash can be recommended as low cost adsorbent for removal of both arsenic and fluoride from contaminated water.

#### Materials and method :

*Collection of fly ash sample* : Fly ash sample was collected from Bandel Thermal Power Plant, Triveni, Hooghly, West Bengal. The sampling procedure is described elsewhere<sup>4</sup>. It was sieved to different mesh sizes. The particles passing through the sieve were collected. It was washed with hot distilled water several times, dried at 100 °C and kept in a desiccator.

*Preparation of stock solute solutions* : Stock solution (1000 mg dm<sup>-3</sup>) of As<sup>V</sup> was procured from E. Merck, Germany. Required experimental solutions of different concentrations were prepared by exact dilution and made acidified with H<sub>2</sub>SO<sub>4</sub> to keep As<sup>V</sup> predominantly as H<sub>3</sub>AsO<sub>4</sub>. Arsenic concentration was measured spectrophotometrically using silver diethyldithiocarbamate at a  $\lambda_{\max}$  of 520 nm<sup>17</sup>. Fluoride solutions in the required concentration range were prepared by exact di-

**Table 3.** Thermodynamic constants for the solutes

Temp. (K)	Arsenic			Fluoride		
	$-\Delta G$ (kcal)	$-\Delta H$ (kcal)	$\Delta S$ (cal)	$-\Delta G$ (kcal)	$-\Delta H$ (kcal)	$\Delta S$ (cal)
323	2.82			3.04		
313	2.80	5.38	8.04	3.13	5.74	8.38
303	2.97			3.21		

lution of stock solution ( $50 \text{ mg dm}^{-3}$ ) of sodium fluoride (E. Merck, India). The quantitative analysis of the fluoride ions in the sample was done using SPADNS spectrophotometric method at a  $\lambda_{\text{max}}$  of  $535 \text{ nm}$ <sup>17</sup>.

**Procedure** : Batch mode adsorption experiments were performed in a thermostated shaker with  $50 \text{ cm}^3$  solute solution with respective dose of fly ash at a definite particle size. The solute concentration remained in the solution after equilibration was estimated spectrophotometrically<sup>17</sup>. Effect of pH was studied by adjusting the initial pH of solution to different values between 2.0 and 10.0 with dilute NaOH and HCl solutions. Isotherm study was carried out with different initial solute concentrations  $2\text{--}10 \text{ mg dm}^{-3}$  after agitating up to equilibrium time. It was found that there was no adsorption due to the container walls. The containers were kept sealed throughout the duration of tests. Experiments were carried out in triplicate and the percent error was calculated.

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