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Adsorptio-Remediation Of Fluoride By Municipal Solid Waste Ashes

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ABSTRACT

The results of utilization of municipal solid wastes as adsorbents for the remediation of fluoride ions in water are presented. It concerns with the removal of fluoride ions by adsorption by water insoluble solid waste-ashes. The pH was maintained at 5.328 in order to prevent the masking of fluorides by other species. The adsorption abilities as a function of contact time, pH, sorbent concentration and temperature was investigated. They obey the Freundlich, Langmuir and Lagergren adsorption isotherms. To evaluate the kinetics data of the adsorption process, a series of time-dependent, and pH dependent adsorption studies were used. The adsorption processes follow simple first order kinetics in the sorbate concentration for a given amount of residential and market solid waste ashes. As pH increases from acidic range, the adsorptivity increases, reaches a maximum at neutral pH and then again decreases. This is attributed to the pH-dependent surface characteristics of the solid waste powder-ashes and to the pH-dependent speciation details of the adsorbent system.

Keywords: Contents of fluoride, Adsorption, Isotherm, Solid waste ashes, Rate constant.

INTRODUCTION

Efforts of scientists are needed to minimize the Fluoride and heavy metal water pollution. To protect of health from dental fluorosis and skeletal fluorosis, the removal of fluoride from drinking water is very essential. Some of the standard methods for fluoride removal include adsorption and coagulation or co-precipitation followed by sedimentation. Lime or alum is the commonly used coagulant. Calcium phosphate is used as the co-precipitant. Activated alumina is the most popular and most effective adsorbent to reduce fluoride concentration to a permissible level, because of its ease of application and cost-effectiveness [1-3]. An alumina reacts with fluoride ions and form alumino fluoro complexes. These complexes are unstable in neutral or alkaline pH regions [4]. Consequently, the role of pH in minimizing alumina dissolution as opposed to maximizing fluoride removal has also been considered. Upon hydration, hydroxo groups develop at the alumina surface. These hydroxo groups behave amphoterically.

Now-a-days effluent treatment and waste water disposal are always challenging tasks for the industries. In developing countries the high cost of activated carbon, inhibits its large scale use as an adsorbent [5-7].

Low cost activated carbons were prepared and used for Defluoridation of potable water[8]. Hence, we present the use of low-cost residential waste ash and market waste ash as fluoride ion sorbents. These ashes were soaked in double distilled water and dried in the oven at above 500 ^{0}C for 24 hours. This was done by several times. These dried ashes were found to be good adsorbents for the heavy metal water pollution. This paper discusses the methods of removal of fluoride by residential waste (RW) and market waste (MW) ashes from aqueous systems. The pH was maintained at 5.328 in order to prevent the masking of fluorides by other species.

MATERIALS AND METHODS

Buffers of varied pH's were prepared for the purpose of our studies. A series of stock solutions was prepared by combination of the members of which, set of desired pH's was obtained. The Orion Cat. No.810007(3M KCl) was used as internal filling solution and Orion Cat. No.810007 (1g KCl in 200 ml distilled water which pH is 7) was used as storage solution for pH electrode. Always used fresh buffers (pH=4.02 and pH=9.40) were used for calibration. Orion Cat. No.9409BN electrode was used for the determination of fluoride. The fluoride reference electrode Model 90-01 was filled with Orion Cat. No.900001solution. The contents of fluoride were measured by ion-selective electrodes. It is accurate even upto $1X10^{-6}$ M level. The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species [7].

To a 50 ml of 5 ppm fluoride solution was added 0.0502 g of the adsorbent and the contents were shaken in a rotatory shaker for a period of one hour. Then 25 ml of the supernatant liquid was decanted into a beaker and 2.5 ml of TISAB (Total Ionic Strength Adjustment Buffer) solution of pH=5.5 was added and (if required the pH was slightly adjusted with dil. HCI) its fluoride concentration was measured. When the pH<4.5, hydrogen ions react with fluoride electrode and the electrode responds to other ions, such as OH^- and $HC0_3^-$. Consequently, the electrode potential reading could be higher than that obtained when only fluoride ions are present [9].

RESULTS AND DISCUSSION

Effect of Sorbent Dosage: From figure 1**,** it is evident that for the quantitative removal of 5.12 mg L^{-1} in 25 ml**,** a minimum sorbent dosage of 50 mg of both ashes is required. The decrease in unit adsorption with increase in the dose of the sorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction.

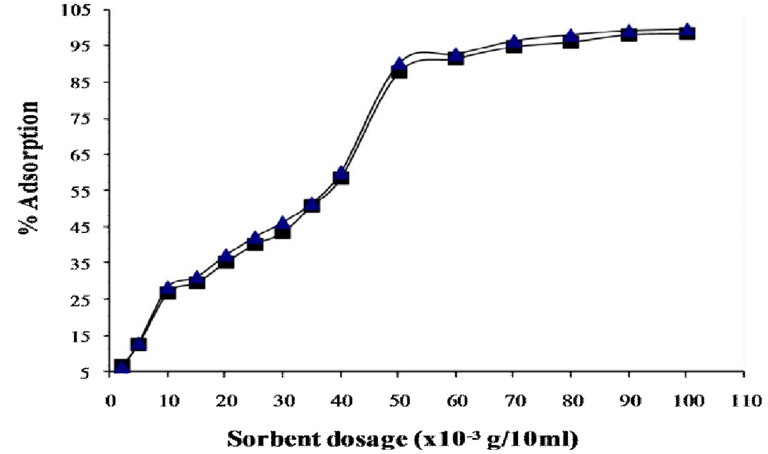

Figure1: Effect of sorbent dosage on the adsorption of fluoride (5.12 mg) on MW ash (Δ) and RW ash (□) at pH = 5.51 and at 30 ºC.

Effect of Initial Concentration : It revealed that from figure 2 and 3 the effect of agitation time as well as the concentration on the removal of fluoride was 6.75 mg g^{-1} (67.5%) by market waste ash and 6.023 mg g^{-1} (60.23 %) in the case of residential waste ash, at pH = 5.5. Moreover the equilibrium was attained in about one hour.

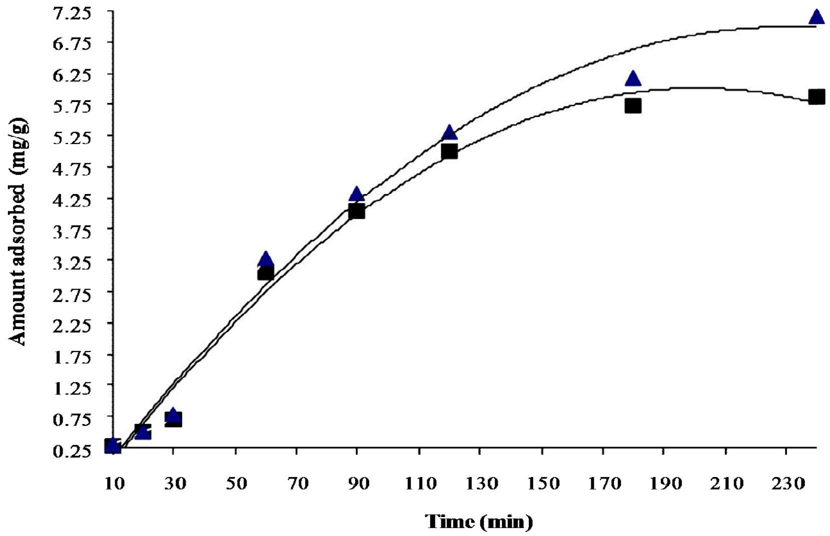

Figure 2: Effect of time on the adsorption of fluoride (1.028 mg L^{-1}) on MW ash (Δ) and RW ash (□) at pH = 5.51 and at 30 ºC (50 mg).

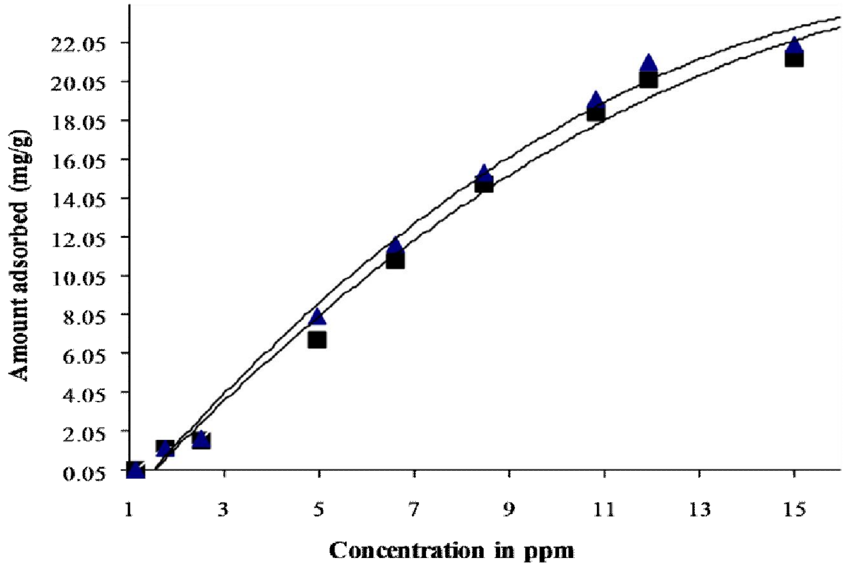

Figure 3: Effect of initial concentration on the adsorption of fluoride (1.028 mg L^{-1}) with MW ash (Δ) and RW ash (□) at pH = 5.51 and at 30 ºC (50 mg).

Effect of pH: In Figure 4**,** it is shown how the adsorption of fluoride ions into hydrous solids is affected by pH. The amount of fluoride adsorption increases with increasing pH until a maximum is reached at pH=5. It then decreases with further increase in pH. The results are in line with those reported by others [10-12].

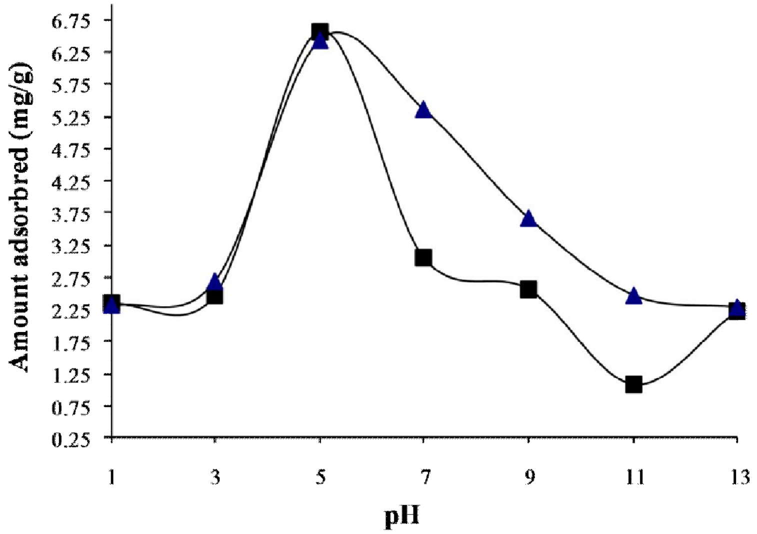

Figure 4: Effect of pH on the adsorption of fluoride (1.028 mg L^{-1}) with MW ash (Δ) and RW ash (□) at pH = 5.51 and at 30 ºC (50 mg).

The Kinetics of Adsorption of fluoride on RW and MW ashes was studied by using Legergren's equation

$$\log(q_e - q) = \log q_e - \frac{k_r t}{2.303}$$

In figure 5, the linearity of curve indicates the validity of the Legergren's equation for the present system at room temperature and determined the k_r value. This suggests that the process follows first order kinetics. From the slope of the plot the values of K_r are calculated and they are found to be 8.5211 X 10^{-3} and 8.9817 X 10^{-3} min-^{1} in case of residential waste ash and market waste ash respectively for an initial concentration of 5.245 mg L^{-1} of fluoride.

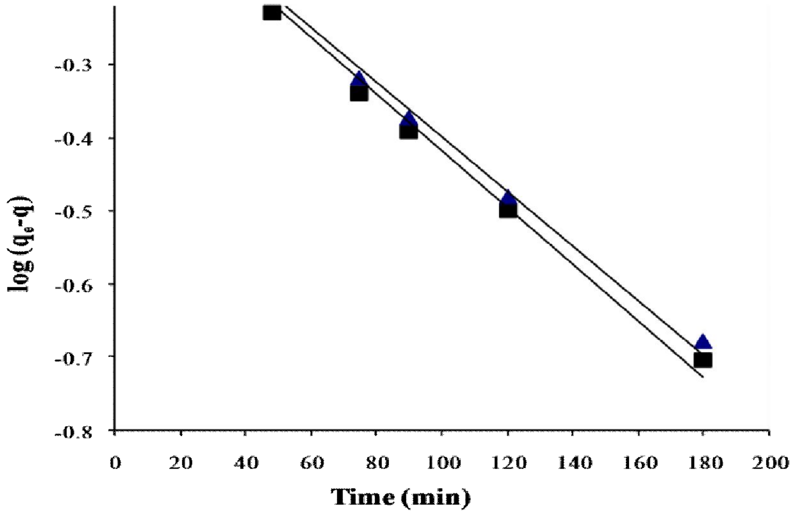

Figure 5: Legergren's plot for the adsorption of fluoride (1.028 mg/L) on MW ash (Δ) and RW ash (□) pH = 5.51 and at 30 ºC (50 mg).

Adsorption Isotherms: The adsorption isotherms have been of great importance in the waste water treatment by adsorption technique. It provides approximate estimation of the adsorption capacity of the adsorbents. It is evident from the studies carried out, that the market waste and residential waste ashes are potential adsorbents of fluoride ions. From figure 5**,** is clear that the adsorption of fluoride on the waste ashes attains equilibrium.

Freundlich Isotherm: The adsorption data were fit for the Freundlich equation,

$$\log(q_e) = \log(k_r) + \frac{1}{n}\log(C_e)$$

where q_e is the amount of fluoride adsorbed per unit mass of the sorbent after the equilibrium time, k_f is a measure of adsorption capacity and 1/n indicates the adsorption intensity.

The adsorption of fluoride on market waste and residential waste ashes were fit in the Freundlich adsorption isotherm. The data pertaining to figure 6 and 7 are given in table 1**.** The adsorption capacity of market waste ash is slightly greater than that of residential waste ash.

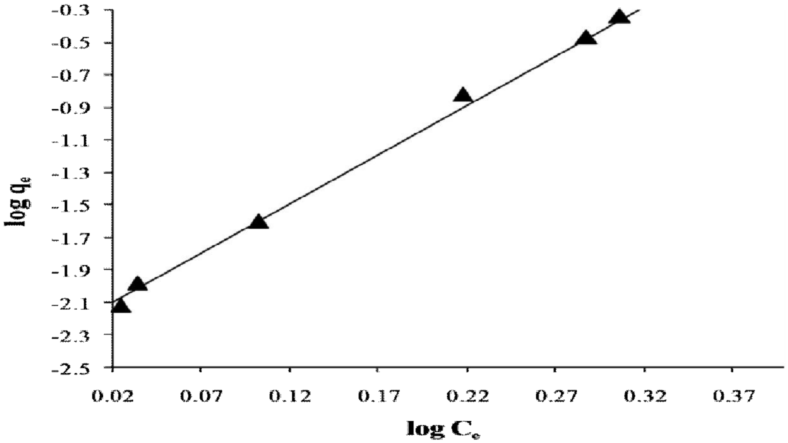

Figure 6: Freundlich adsorption isotherm for fluoride (1.028 mg L^{-1}) on MW ash (50 mg) at pH = 5.51 and at 30 ºC.

Table 1: Freundlich constants for the adsorption of fluoride on waste ash at room temperature (30 ºC).

Name of the waste ash	1/n value	K_f value
Residential waste ash	7.33775	3.1003
Market waste ash	6.0487	2.216

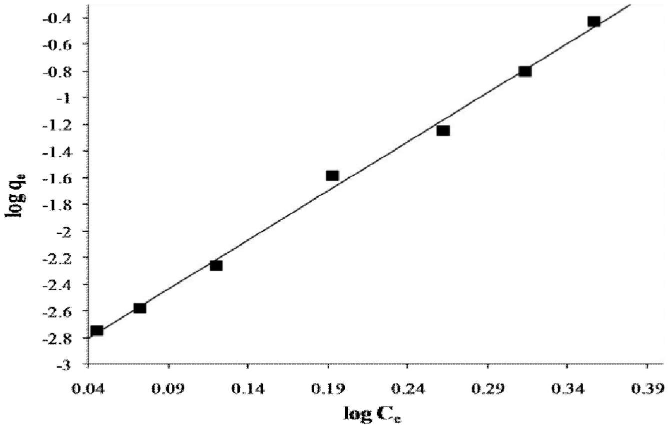

Figure 7: Freundlich adsorption isotherm for fluoride (1.028 mg L^{-1}) on RW ash (50 mg) at pH = 5.51 and at 30 ºC.

Langmuir Isotherm : The equilibrium data for removal of fluoride on market waste ash and those on residential waste ash at room temperatures were also fit into the Langmuir adsorption isotherm,

$$\frac{C_e}{q_e} = \frac{1}{K_L} b + \frac{C_e}{b}$$

where C_e is the equilibrium concentration of fluoride, q_e is the amount adsorbed at equilibrium in mg g^{-1}, k_L is Langmuir equilibrium constant and b is Langmuir adsorption capacity respectively. The equilibrium data for the removal of fluoride on market waste ash and those on residential waste ash at 30°C was fit in to the Langmuir adsorption isotherm and shown in figure 8 for market waste ash and figure 9 for residential waste ash, data is given in table 2. The linearity of these plots indicates the applicability of Langmuir adsorption isotherm for the present adsorption process.

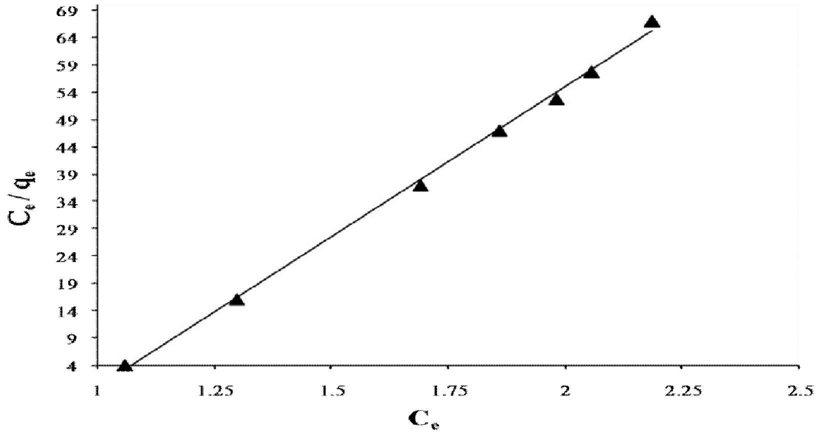

Figure 8: Langmuir adsorption isotherm for fluoride (1.028 mg L^{-1}) on MW ash (50 mg) at pH = 5.51 and at 30 ºC.

Table 2: Langmuir constants for the adsorption of fluoride on waste ash at room temperature (30 ºC)

Name of the waste ash	b value	K_L value
Residential waste ash	0.017453	3712.2
Market waste ash	0.017705	3229.59

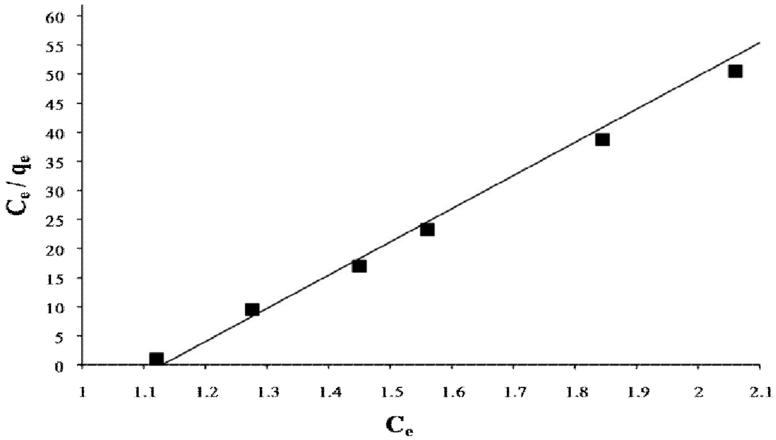

Figure 9: Langmuir adsorption isotherm for fluoride (1.028 mg L^{-1}) on RW ash (50 mg) at pH = 5.51 and at 30 ºC

APPLICATIONS

As the results indicate the market waste and residential waste ashes usage may be promoted as good adsorbents of fluoride ions in drinking water to protect our health from fluorosis. These ashes are no-cost and eco-friendly materials.

CONCLUSIONS

The adsorption capacity of market waste ash is slightly greater than that of residential waste ash. It is also clear that the adsorption of fluoride on the waste ashes attains equilibrium. It is evident from the studies carried out that the market waste and residential waste ashes are potential adsorbents of fluoride ions.

REFERENCES

[1] D.Clifford, J. Motson and R.Kennedy, *Indian Water Engineering* **1978**, 12, 17.
[2] F. Rubel and R.D.Woosley, *Journal of American Water Works Association* **1979**, 45, 71.
[3] K.R.Hall, L.C.Eagleton, A.Acrivos and T.Vemeulen, *Industrial Engineering Chemical Fundamentals* **1966,** 212, 5.
[4] Alan Chappell and Deve Block, *International Journal of Biocycle*, **1998**, April, 54.
[5] A.N. Gopalakrishnan and V.Mohan, *Indian Journal of Environmental Protection*, **1997**, 268, 17.
[6] G.Sarala Devi, *Studies of Chemo-and Adsorptio-Remediation of Heavy Metal Water Pollution and Investigations of some Metal-Drug Interactions*, a Ph.D. thesis submitted to Regional Engineering College, Kakatiya University, Warangal, A.P., India, **1998**.
[7] S.A.Chung and C.S.Poon, *Waste Management & Research*, **1994**, 21, 12.
[8] K.Somasekhara Rao,B.V.R.Reddy and Ch. chakrapani, Activated KAZA's Carbons-Defluoridation of Potable Water, LAP Lambert Academic Publishers, Germany, **2011**.
[9] E.A.Savinelli and A.P.Black, *Journal of American Water Works Association*, **1958**, 60, 33.
[10] S.K.Srivatsav, R.Tyagi and N.Pant, *Water Research*, **1989,** 1161, 9.
[11] C.Raji and T.S. Anirudhan, *Indian Journal of Chemical Technology*, **1997,**157, 4.
[12] C.R.N.Rao, L.Iyengar and C.Venkogachar, *Journal of Environmental Engineering, ASCE*, **1989,** 369, 119.