FLY ASH AND MAIZE husk fly ash AS AN ADSORBENT FOR REMOVAL OF FLUORIDE

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Abstract

Fluorine, a fairly common element of the earth's crust, is present in the form of fluorides in a number of minerals and in many rocks. Excess fluoride in drinking-water causes harmful effects such as dental fluorosis and skeletal fluorosis. Fluorine forms diatomic molecules that are gaseous at room temperature. The density is about 1.3 times that of air. Though sometimes cited as yellow-green, fluorine gas is actually a very pale yellow. Its color can only be observed in concentrated fluorine gas when looking down the axis of long tubes. It appears transparent when observed from the side in normal glass tubes or if allowed to escape into the atmosphere. The element has a "pungent" characteristic odor that is noticeable in concentrations as low as 20 ppb.

Fluorine condenses to a bright yellow liquid at −188 °C (−307 °F), close to the condensation temperatures of oxygen and nitrogen. Fluorine solidifies at −220 °C (−363 °F) into a cubic structure, called beta-fluorine. This phase is transparent and soft, with significant disorder of the molecules. At −228 °C (−378 °F) fluorine undergoes a solid–solid phase transition into a monoclinic structure called alpha-fluorine. This phase is opaque and hard with close-packed layers of molecules. The solid state phase change requires more energy than the melting point transition and can be violent, shattering samples and blowing out sample holder windows. In general, fluorine's solid state is more similar to oxygen than to the other halogens.

Keywords:. *Fluoride , Maize husk ,fly ash, adsorbent*

1. Introduction

Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking-water. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. The high fluoride level in drinking water has become a critical health hazard of this century as it induces intense impact on human health including skeletal and dental fluorosis. Though fluoride is an essential constituent for both humans and animals, it can be either beneficial or detrimental to human health depending on the level of fluoride in drinking water. In India, this problem is common in places such as Andhra Pradesh, Tamilnadu, Karnataka, Kerala, Rajasthan, Gujarat, Uttar Pradesh, Punjab, Orissa and Jammu and Kashmir.

The free fluoride level in drinking water was identified at 3.02 mg/L in Kadayam block of Tamilnadu. A fluoride survey in Nilakottai block of Tamilnadu showed a positive correlation between the prevalence of dental fluorosis in children and levels of fluoride in portable water is 3.24 mg/L. Adsorption is one of the significant techniques in which fluoride is adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles. Many natural and low cost materials such as red mud, zirconium impregnated coconut shell carbon, cashew nut shell carbon, ground nut shell carbon and clays have been used as adsorbents for fluoride removal from drinking water. Recently, amorphous alumina supported on carbon nano tubes, aligned carbon nano tubes, ion exchange polymeric fiber, and an ion exchanger based on a double hydrous oxide of Al and Fe ($Fe_2O_3Al_2O_3 \times H_2O$) have been assayed for removing fluoride from drinking water as well as industrial wastewater. Thus, it is important to develop or find cheaper adsorbents for fluoride removal from water that have greater fluoride adsorption capacities like the above said adsorbent

2. SCOPE OF THE STUDY

Both quality and quantity of water supply plays a significant role for the protection of public health. The need for the improvement of surface water supply on which the majority of the rural population in developing countries still depends is well recognized. Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking-water. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. It is a challenging task though a feasible solution to introduce the traditional purification methods such as the use of low cost adsorbents. Researchers have found out many natural adsorbents to treat water and many of them are used all over the world. In the present study the fly ash obtained from thermal power plant and the fly ashes obtained from Maize husk are used as adsorbents which are not popular in India even though they are in abundant quantity all over the country.

The study was undertaken along the following lines.

1. Performance evaluation of Thermal power plant fly ash (TPP fly ash) and Maize husk fly ash(MH fly ash) in Batch study, in terms of fluoride , by carrying out the experimental work for five different parameters, viz. Contact time, p^H, Adsorbent dose, Stirring rate and Initial fluoride concentration.
2. Optimization of both the adsorbents for the five parameters varied, to obtain maximum efficiency of fluoride removal from water. The scope of this phase of the study is to reduce the fluoride level, so that the ill

effects due to fluoride concentration can be reduced.

3. Infra red Spectra study to probe into the nature of the adsorbing action of both the fly ash used.

Validation of the results obtained, in terms of fluoride removal efficiency (percentage), using adsorption isotherms, viz. Langmuir, Freundlich, Temkin and Redlich- Perterson isotherm mo Table **3**.

Chemical analysis of TPP fly ash and MH fly ash

Constituent (Chemical characteristics)	TPP Fly ash	Maize Husk Fly ash
	Amount (%)	Amount (%)
SiO_2	52.70	38.33
k_2O	---	27.58
CaO	7.20	7.83
MgO	---	5.01
P_2O_5	---	4.53
Cl	---	3.02
SO_3	---	1.72
Fe_2O_3	8.40	0.47
Al_2O_3	21.90	0.22
LOI	9.10	11.4

4. METHODOLOGY

Experimental work of this study has been divided into following phases. They are

• Adsorbance procedure by Batch study.

1. Effect of contact time on fluoride removal.
2. Effect of p^H on fluoride removal.
3. Effect of Adsorbent dose on fluoride removal.
4. Effect of stirring rate on fluoride removal.
5. Effect of initial fluoride concentration (IFC) on fluoride removal.

• Validation of results through Modeling (Langmuir, Freundlich, Temkin, Redlich-perterson Models) for fluoride removal

3 THE ADSORPTION ISOTHERMS

Four isotherm models were used to fit the experimental data namely: Langmuir model, Freundlich model, Temkin Model and Redlich-Perterson Model. Langmuir, Freundlich model, Temkin Model and Redlich-Perterson Model were chosen to describe the adsorption equilibrium.

Freundlich, Langmuir, Redlich-Perterson and Temkin isotherms were plotted to provide deep insight to the adsorption of fluoride on Thermal Power Plant fly ash and Maize husk fly ash. The isotherms not only provides the general idea of the effectiveness of the Thermal Power Plant fly ash and Maize husk fly ash in removing fluorides, but also indicates the maximum amount of fluoride ions that will be adsorbed by the Thermal Power Plant fly ash and Maize husk fly ash. However, adsorption isotherms are equilibrium tests and thus do not indicate the actual performance of the adsorbent.

Langmuir isotherm is valid for single-layer adsorption [51]. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface.

The linear form of the Langmuir isotherm is expressed as follows.

$$1/qe = 1/QO + 1/\ QO\ b\ Ce$$

Where, qe (mg/g) is the ratio of fluoride adsorbed to the dosage of the adsorbent, Ce (mg/l) is the equilibrium concentration of adsorbate, QO is the adsorption capacity of adsorbent and b is a constant related to the energy adsorption.

The values of Langmuir constants (slope) and adsorption capacity (intercept) were obtained from the linear correlation plots between 1/qe and 1/ Ce.

The Freundlich equation is basically empirical but is often useful as a means for data description. It generally agrees quite well with the Langmuir equation and experimental data over moderate ranges of concentration [51].

The linear form is represented by the following equation.

$$\ln qe = \ln Kf + 1/n \ln Ce$$

Where Kf is the adsorption capacity of adsorbent and n is a constant related to the intensity of adsorption. For 1/n less than unity, adsorption is the predominant process taking place otherwise desorption becomes predominant. The values of Freundlich constants (slope) and adsorption capacity (intercept) were obtained from the linear correlation plots between ln qe with ln Ce.

The Temkin isotherm [40], the simple form of an adsorption isotherm model, has been developed considering the chemisorption of an adsorbate onto the adsorbent, is represented as:

$$qe = a + b\log ce$$

where *q*e and *c*e have the same meaning as noted previously and the other parameters are called the Temkin constants. The plot of *q*e *versus* log *c*e will generate a straight line. The Temkin constants *a* and *b* can be calculated from the slope and intercept of the linear plot.

The Redlich–Peterson isotherm [40] contains three parameters and incorporates the features of the Langmuir and Freundlich isotherms.

The linear form is represented by the following equation.

$$\ln((A\ Ce/qe)-1) = g \ln Ce + \ln B$$

4.RESULTS AND DISSCUSSION

Results obtained from the experimental work carried out in the following phases, are presented in tabular and graphical form and a detailed discussion of the results follows each phase of the experimental work given as below.

1) Adsorption procedure by Batch study.
   a) Effect of contact time on fluoride removal efficiency.
   b) Effect of p^H on fluoride removal efficiency.
   c) Effect of adsorbent dose on fluoride removal efficiency.
   d) Effect of stirring rate on fluoride removal efficiency.

e) Effect of initial fluoride concentration (IFC) on fluoride removal efficiency.

2) Validation of results through Modeling (Langmuir, Freundlich, Temkin, Redlich-perterson Models) for fluoride removal.
3) Infra Red (IR) Spectra Study to determine the presence of adsorption friendly functional groups in two adsorbents used.

4) for 120 minutes in case of both the adsorbents.
5) The uptake of fluoride ions is possible between p^H of 2.0 and 12, however, p^H of 2 gives maximum fluoride removal efficiency (71.71% for MH fly ash and 72.71% for TPP fly ash), since neutralization of OH^- ions by large number of H^+ ions takes place at less p^H values for both TPP fly ash and MH fly ash.
6) In case of both the adsorbents used, the percentage of fluoride removal was found to be a function of adsorbent dose and contact time at a given initial solute concentration. In case of effect of adsorbent dose, equilibrium dosage of 2g was found in case of both the adsorbents used. While the maximum efficiency was found to be 87.14% and 86% for TPP fly ash and MH fly ash respectively.
7) For Stirring rate variation, the equilibrium stirring rate of 200 rpm and 250 rpm was found for TPP fly ash and MH fly ash respectively. The maximum efficiency obtained was found to be 86.85% and 84.71% for TPP fly ash and MH fly ash respectively.
8) As for both TPP fly ash as well as MH fly ash, the removal efficiency

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