Defluoridation Kinetics over Lime Stone Slurry Impregnated Fly Ash

Chemistry

KEYWORDS: Fluoride, Adsorption kinetics, LSFA catalyst

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ABSTRACT

The adsorption kinetics of the removal of fluoride (F-) from water over lime stone slurry impregnated fly ash (LSFA) catalyst using batch mode has been investigated in the present study. BET surface area, XRF, XRD, FTIR and SEM techniques were used to characterize the physico-chemical attributes (crytallinity, determination of calcium and magnesium silicate phases, morphology) of the catalyst. Adsorption data were modelled using the Freundlich and Langmuir adsorption isotherms and followed first order kinetic equation. The present research includes assessment of a new adsorbent generation, process optimization and a cost benefit process.

Introduction

Management of ions hazardous to health, such as fluoride (F-), is of interest for public health. Fluorine is a naturally occurring element in minerals, geochemical deposits and natural water systems and enters food chains through either drinking water or eating plants and cereals [1]. It is also beneficial in human body for the calcification of dental enamel and maintenance of healthy bones when present within the permissible limit. But excess intake of fluoride is responsible for dental caries, bone fluorosis, and lesions of the thyroid, endocrine glands, and brain. According to the World Health Organization (WHO), the tolerance limit of fluoride content of drinking water is 1.5 mg/l [2].

Treatment of wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration, precipitation, nanofiltration, ion-exchange, electrocoagulation flotation and adsorption have been used for fluoride removal [3]. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations.

In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic, and biomass materials such as activated alumina, alum sludge, chitosan beads, red mud, zeolite, calcite, hydrated cement, attapulgite and acid-treated spent bleaching earth [4]. These adsorbents have shown a certain degree of fluoride adsorption capacity but some of them can only be used in a narrow pH range (5-6) and some of them are too expensive to be considered for full-scale water treatment. Furthermore, most of them are fine particles or powders which would be suspended in water, making separation difficult. Therefore, an effective and low-cost adsorbent is desired as an efficient treatment technology for fluoride removal in large scale water samples.

Till now many adsorbents for F- removal from water solutions have been developed using Cu or by impregnating Al, La and Zr on various other adsorbents. All these adsorbents have a limitation that during adsorption there is a possibility that the coated elements may leach out in the treated water and can make it unfit for drinking purpose [5].

In this regard, the present work elaborates the synthesis of a new type of adsorptive catalyst, generated from fly ash impregnated by lime stone slurry waste, having more adsorptive efficiency for fluoride removal comparable to other costly adsorbents. Fly ash consists of silica, alumina, iron oxide, lime, magnesia and alkali in varying amount with some unburnt activated carbon [6] and possess large surface area together with their surface chemical structure allows them to be used in a wide variety of industrial applications, in agriculture, in metal recovery, in water and atmospheric pollution control [7]. On the other hand, new solid waste lime stone slurry containing high amount of calcium and magnesium content, is produced in huge quantity from Kota stone industries. For this purpose, abundant availability of both solid wastes inspired us to develop low cost, effective adsorbent material for removal of fluoride from drinking water, which is mainly ground water in large portion of rural areas in Rajasthan. Batch adsorption studies are carried out systematically in terms of process parameters such as initial concentration of fluoride ion. Adsorption data are applied on Langmuir and Freundlich adsorption isotherms. Various kinetic models are tested to find out the suitable one to represent fluoride removal kinetics over LSFA catalyst.

MATERIALS AND METHODS

A. Materials

Fly ash (Class F type) having SiO_2 (58%), Al_2O_3 (19%), Fe_2O_3 (8%), CaO (0.6%), MgO (0.6%), TiO_2 (1.3%), Na_2O (2.8%) and trace elements (4.1%) analyzed by X-ray fluorescence spectrometer was collected from Kota Super Thermal Power Station (Kota, Rajasthan, India). Lime stone slurry waste was procured directly from stone cutting industries at Kota. MgF_2 were purchased from s.d. Fine Chem. Ltd., India and were used as such.

B. Catalyst Synthesis

The adsorption catalyst was synthesized by mixing fly ash and lime stone slurry in a fixed ratio of 3:1. The mixture was stirred continuously at 30 ºC for 24 h. The mixture was then filtered and dried at 100 ºC for 24 h to remove excess water. The dried material was milled in mortar for one hour for uniform sizing and increasing surface area. This material was finally calcined at 550 ºC for 6 h.

C. Experimental Procedure

The stock solution of 100 mg/l fluoride was prepared by dissolving 5 g of anhydrous MgF_2 in 100 ml of distilled water. Fluoride removal studies were conducted using batch method. In which, a fixed amount of adsorbent LSFA (0.5 g), was added to 100 ml of fluoride solution of varying concentration (2, 6 and 10 mg/l) taken in stoppered conical flasks, placed in a thermostated agitation (30 ºC) assembly. The solution was agitated continuously (600 rpm) at constant temperature. The adsorbate uptake q_e (mg/g), was calculated using equ.(1)

$$q_e = \frac{C_o - C_e}{W} x V \qquad \text{.................. (1)}$$

Where C_0 is the initial adsorbate concentration (mg/l), C_e is the equilibrium adsorbate concentration in solution (mg/l), V is the volume of the solution, and W is the mass of the adsorbent (g) and q_e is the amount of adsorbed fluoride.

The kinetics was followed by withdrawing 0.5 dm^{-3} aliquot samples at different intervals. The adsorbent was separated from aliquot by filtration through Whatman no. 42 filter paper. Residual concentration of fluoride ion was estimated using ion meter with fluoride ion selective electrode. Experimental runs were observed with initial rapid adsorption trends.

D. Catalyst characterization

The chemical components of the pure fly ash were analyzed by X-ray fluorescence Spectrometer (Philips PW1606). The BET surface area was measured by N_2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer. The FTIR (Fourier transform infrared) spectra of different samples were recorded using a Bruker FTIR spectrophotometer (Tensor-27) with DRS by mixing the sample with dried KBr (in 1/20 wt. ratio) in the range of 550-4000 cm^{-1} with a resolution of 4 cm^{-1}. Powder X-ray diffraction studies were carried out by using (Philips X'pert) analytical diffractometer with monochromatic CuK_α radiation (k = 1.54056 Å) in a 2θ range of 0-80°. The morphological and textural studies of the catalysts were performed by Scanning electron microscopy (Philips XL30 ESEM TMP).

Result and Discussion

The XRD and SEM results of the raw fly ash have been reported earlier in our literature data [8]. In Fig. 1, the XRD pattern of LSFA catalyst indicates the presence of calcium silicate (31°, 32°, 37°, 47°) and magnesium silicate (36°, 43°) phases [9, 10]. The SEM image of LSFA catalyst (Fig. 2) shows dense particles with distribution of varying particles size deposited lime stone slurry, with clearly visible on the external surface of fly-ash particles. The specific surface areas of KTPS fly ash and LSFA catalyst are found to be 8 and 7 m^2/g respectively.

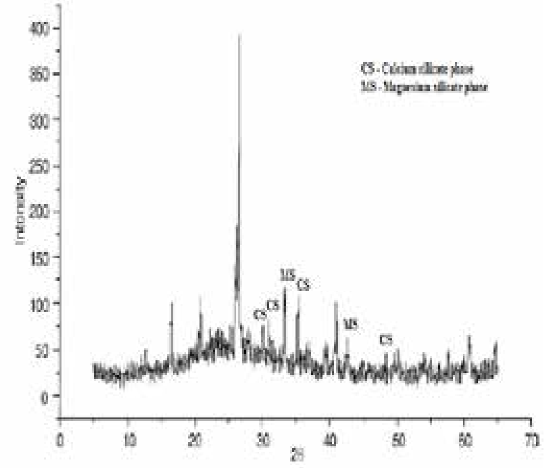

Fig.1 XRD of LSFA catalyst

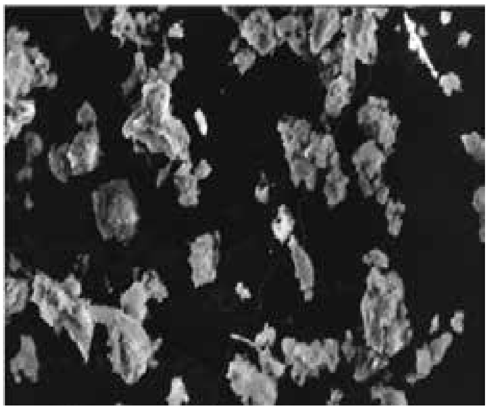

Fig. 2 SEM image of LSFA catalyst

Adsorption Isotherm Analysis

The adsorption data were analysed with the help of the following linear forms of Freundlich and Langmuir isotherms [11, 12]:

Freundlich isotherm

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{............(2)}$$

Langmuir isotherms

$$\frac{1}{q_e} = (1/Q_0) + (1/bQ_0C_e) \qquad \text{.............(3)}$$

where q_e is the amount of adsorbed F^- per unit weight of LSFA(mg/g), K_f and 1/n are freundlich constant related to adsorption capacity and intensity respectively, C_e is the concentration of fluoride (mg/l) at equilibrium, Q_0 is the maximum adsorption at monolayer coverage in (mg/g), b is the Langmuir constant in mg/l.

The adsorption isotherms parameters along with the correlation coefficients for the various concentration of F^- are presented in Table-1 which indicates a smaller value of 1/n at 10 mg/l of F^-, points out a better adsorption mechanism and formation of relatively stronger bond between F^- and LSFA catalyst. The observed statistically significant (at 95% confidence level) linear relationships as evidenced by the r-values (close to unity) indicate the applicability of these two adsorption isotherms and the monolayer coverage on adsorbent surface. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by,

Table-1 Values of Langmuir and Freundlich constants over LSFA = 0.1 gmdm-3 at different concentration of F-

[F-]	Langmuir Constants				Freundlich Constants		
mg/l	b	r	Q0	R2	Kf	1/n	R2
2	0.9170	0.052	45.248	0.9576	1.0642	0.1103	0.9624
6	0.2969	0.035	126.58	0.9567	0.2132	0.1068	0.9620
10	0.1736	0.370	185.18	0.9597	1.3536	0.0978	0.9892

$$r = 1/1 + b \ \ C_o \qquad \text{........(4)}$$

r, a dimensionless constant separation factor, whereas, C0 is the highest fluid-phase concentration (mg/l). The different types of isotherms can be described on the basis of r values (r = >1 unfavorable, r = 1 linear, r < 0, r < 1 is favorable and r = 0 irreversible). It is clear from Table-1 that the r values for the present experimental plots are in the range of 0.05 to 0.37, which favors the adsorption of MgF2 on LSFA catalyst.

Adsorption kinetic studies

The adsorption data were used at five different kinetic models using least square regression analysis for different initial concentration of fluoride. On the basis of high R2 and low SEE, the most favorable model for fluoride adsorption kinetics is the first order at 2, 6 and 10 mg/l [F-] in Fig.3, while two-rate constant and Elovich equation are completely rejected.

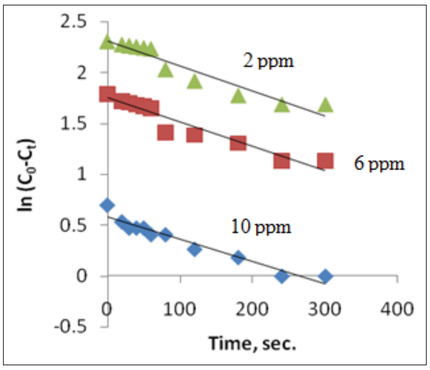

Fig.3 First order equation plots at different [F-]
[LSFA] =0.5gdm-3, temp=300C.

The values of slope, correlation coefficient (R2), and standard errors of estimate (SEE) at 10 mg/l [F-] are given in Table-2 which indicates that the correlation coefficient value for the first-order kinetic model (R2 = 0.9211) is higher than that obtained from the other kinetic models.

Table-2 Coefficient of determination (R2), standard error of estimate (SEE), and slope values for different Kinetic models at 10 mg/l of [F-].

Kinetic Models	R^2	SEE	Slope
Zero Order $C_0 - C_t = a\text{-}bt$	0.888	0.634	-0.018
First order $\ln(C_0 - C_t) = a\text{-}bt$	0.921	0.074	-0.002
Elovich Equation $C_t = a - b \ln t$	0.698	0.548	1.949
Parabolic diffusion $C_t = a - b\, t^{1/2}$	0.885	0.666	0.343
Two rate constant $\ln C_t = \ln k + l/m \ln t$	0.023	0.323	1.176

Conclusion

The LSFA catalyst examined in this study showed promising properties as a low-cost and effective adsorbent for the removal of fluoride from water. The adsorption kinetic data followed first order rate model and adsorption equilibrium data followed Freundlich and Langmuir isotherm model with a better fit. The impregnated lime stone slurry was not leached during the adsorption process.

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