STATISTICAL OPTIMISATION OF DEFLUORIDATION USING CALCIUM IMPREGNATED ACTIVATED SLUDGE AS AN ADSORBENT: BATCH STUDY AND MATHEMATICAL MODELING

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Abstract - In this investigation, the de-fluoridation in water was investigated by using calcium impregnated activated sludge .Here activated sludge was the precursor for the preparation calcium impregnated activated sludge. The effect of chemically modified Ca-Activated Sludge(Ca-AS) as an adsorbent was carried out in de-fluoridation study. The different process parameters such as dose of adsorbent, contact time, temperature are optimized by applying two level three factor(2^3) CCD(Central Composite Design) with the help of Design Expert Software in Response Surface Methodology(RSM).Three important process parameters : adsorbent dose (1.0-2.0 g L^{-1}) temperature (35-60 ^{0}C), and contact time(40 -120 min) were selected as the independent variables, while the fluoride adsorption capacities were specified as dependent variables. The higher correlation coefficient(R^2) 0.9762 implies the fitness to the response surface quadratic model.The optimum condition for fluoride adsorption onto Ca-AS was experimented and it was observed respectively 1.0 gL^{-1}, 120 minutes and 60^0C.In this optimized condition the removal efficiency is achieved as 99.31%.

Keywords - Fluoride; Adsorption; Calcium Impregnated Activated Sludge; Response Surface Methodology; Desirability Function

I. INTRODUCTION

Application of fluoride is mostly found in the semiconductor and nano-technology industries as a glass and silica etchant. The source of industrial fluoride are hydrofluoric Acid (HF) ,ammonium bifluoride(NH_4HF). Fluoride has a very high affinity towards calcium (Ca) due to high electronegative character in periodic table.As fluoride is negative ion so it is naturally attracted by positive calcium ion. As a result of high fluoride ingestion by children as well as adults, fluorosis is found in mild version and high version. The fluoride removal from contaminated water is done by adding lime followed by precipitation of fluoride in conventional method[1]. There are various other methods used for the defluoridation of water such as ion-exchange precipitation,reverse osmosis and electro coagulation.WHO recommended that the maximum permissible limit of fluoride in drinking water is 1.5 ppm and highest desirable limit is 1.0 ppm.

By different methods the treatment of waste water[2] is performed by different factory to meet the control values. The sludge[3] is semi- solid type of substance which is left after treatment of industrial waste water. Applying different type of treatment technology, sludge or commonly called industrial waste is generated. But now the problem is the capacity of reclamation plants is saturated, so decreasing industrial waste .In semiconductor plants large amount of waste is discharged. During the treatment of fluoride containing waste water 30 % sludge is generated. Hence, various treatment process is applied for decreasing this industrially generated waste. Here the new technique ,calcium impregnated activated sludge is used for the treatment of fluoride containing waste water.

The main objective of the present study is to determine the optimum conditions for defluoridation by adsorption in aqueous system.The statistical approach by applying experimental study in adsorption mechanism can result in improved product yields, reduced variation in process variables. In this study, the interaction effects of adsorbent dose, reaction time , temperature on defluoridation by calcium impregnated activated sludge were carried out using batch studies and CCD(Central Composite Design) in response surface methodology [4](RSM) .

II. MATERIAL AND METHODS

2.1 Preparation of adsorbent:

- **Chemical Activation**

Sludge was collected from a wastewater treatment unit , then dried in an oven at 105ºC for 24 h. After then it was grinded and stored in a closed vessel .The sewage sludge used in this present investigations was characterized by sufficient amount of inorganic substances as it comes from urban treatment plants. Hence, H_2SO_4 is quite suitable as a chemical activation agent as it can dissolve the majority of inorganic impurities.In this way activated sludge was prepared chemically. Then activated sludge(AS) was the precursor for the preparation of calcium impregnated activated sludge.Then the known quantity of dried and grinded activated sludge was mixed with 25% $CaCl_2$ aqueous solution(w/v) in the specific ratio(5:12).Then the obtained slurry wasrinsed thoroughlywith distilled water several times. The washed slurry was then dried and finallycalcium impregnated activated sludge was collected , kept in Muffle furnace at 500^{o}C. After 30 minutes it was allowed to cool down and taken out. Finally, the Ca- AS was kept in desiccators for experimental study.

2.2 Experimental procedure:
In this study, 100 ml fluoride solutions of concentration 50 mgL^{-1} were taken in 250 mL PTFE conical flasks. The particular weighed amount of adsorbent was added to each solution.Then the flasks were agitated at 150 rpm in anincubator shaker at different temperatures. The effects of contact time, adsorbent dose and reaction temperature on the adsorption of fluoride were studied by using response surface methodology. Experiments were investigated in temperature controlled incubator shaker (INNOVA 4430, New Brunswick Scientific, Canada). Temperature fluctuations in the reactor were negligible. After shaking for particular time intervals those samples were collected from the flasks for analysis of fluoride concentration in the solution. This was estimated by using ion-meter(Thermo Scientific Orion ion-meter, USA).

III. RESPONSE SURFACE METHODOLOGY FOR OPTIMISATION OF ADSORPTION PARAMETERS

The optimum conditions for fluoride adsorption by calcium impregnated activated sludge depends on the three processvariables such as adsorbent dose, temperature and pH of the solution. The percent removal of fluoride is the response of the system. Statistically the prediction of the optimum condition was achieved following the quadratic equation model[5]given below (**Eq. 1).**

$$Y = \beta_0+\sum_{i=1}^{k}\beta i\, xi +\sum_{i=1}^{k}\beta ii\, xi2 +\sum_{i=1}\sum_{j=i+1}\beta ijxixj+ \varepsilon \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here, Y=response (i.e. dependent variable), β_0=constant coefficient, β_i=β_{ii}=β_{ij}=coefficients of linear, quadratic andinteraction effect, x_i and x_j=factors (independent variables)

Andε =error.

Percent removal of fluoride is estimated with a standard RSM design (CCD). The percent removal (%) of fluoride is determined by using the following equation(**2**):

$$R(\%) = \frac{C_i - C_0}{C_i} x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

IV. RESULTS AND DISCUSSION

4.1 Estimation of response surface for maximum fluoride removal:
The maximum fluoride removal was obtained 99.31% at120 min contact time ,at 60 ^{0}C and 1.0 g L^{-1} of adsorbent .The response variable which is expressed as a function of independent variables defined in multiple regression model, developed by Design Expert software is expressed in the form of different numerical factors in equation (3)given below:

Removal % of fluoride (R1)=+97.84 +1.32*A+ 1.92*B +0.88*C– 0.85 * AB- 0.12*AC -0.070*BC -0.75*A^{2}- 0.96*B^{2}– 0.27C^{2}…………………………(3)

$$\frac{\partial R1}{\partial A} = 1.32- 0.85B -0.12C- 1.5A\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

$$\frac{\partial R1}{\partial B} = 1.92 -0.85A -0.07C- 1.92B\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$\frac{\partial R1}{\partial C} = 0.88-0.12A- 0.54C\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(6)$$

$$\frac{\partial^2 R}{\partial A^2} = -1.5; \frac{\partial^2 R}{\partial B^2} = -1.92; \frac{\partial^2 R}{\partial C^2} = -0.54$$

Where A represents adsorbent dose (g L^{-1}),B denotes contact time(min) , C indicates reaction temperature(K) and R1 is the % fluoride removal. For solving partial differential equation(4,5,6) ,the above mentioned equation are equated to zero. Under this condition , A, B, and C were estimated to be 1.02 g, 119.89 min,and 332.8 K, respectively, and % defluoridation obtained to be 99.308%.
It is observed that A, B, C, B^{2}, C^{2}are significant model terms.The fitness of the model was verified by the correlation coefficient (R^2) between the experimental and model predicted values of the response variable. Statistically R^2 value of 0.9762 indicated that the model was statistically significant. A coefficient of variance (2.34x10^{-3}) indicated reliability of the data obtained by performing 20 experiments. Therefore, the model was applied to predict the percentage removal of fluoride in solution within the limits of the experimental factors.

REFERENCES

[1] Ademiluyi F.T. and David-West ISRN E.O., Effect of Chemical Activation on the Adsorption of Heavy MetalsUsing Activated Carbons from Waste Materials, Chemical Engineering, 5 (2012)

[2] Awoyale, A. A., Eloka-Eboka, A. C. and Odubiyi, O. A.,Production and Experimental Efficiency of activated carbon from local waste bamboo for waste water Treatment, International Journal of Engineering and Applied Science,3(2), 8-17, (2013)

[3] Fan, C.-S.; Li, K.-C. Production of insulating glass ceramics from thin film transistor-liquid crystal display (TFT-LCD) waste glass and calcium fluoride sludge. J. Clean. Prod. 2013, 57, 335–341.

[4] F. Ghorbani, H. Younesi, S.M. Ghasempouri, A.A. Zinatizadeh, M. Amini, A. Daneshi, Application of response surface methodology for optimization of cadmium biosorption in an aqueous solution by Saccharomyces cerevisiae. Chem. Eng. J. 145 (2008) 267.

[5] Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillusniger. J Hazard Mater 54:694–702(Amini M, Younesi H, Bahramifar N, Lorestani AAZ, Ghorbani F, Daneshi A, Sharifzadeh M 2008).

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