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Study on Adsorption of Fluoride using Stone Polishing Slurry

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Abstract: Water is contaminated by the dissolution of the minerals and salts from the ground, elimination of waste from the industries and from other sources. One of the contaminations of water is by Fluoride. It may enter into the water by the waste elimination from the industries into the rivers or the streams, by the soil which has high fluoride content in it and from many other sources.In this study the fluoride is removed by the help of the adsorption by stone polishing slurry asadsorbent. Adsorption studies were conducted on the stone polishing slurry as the function of the contact time, dosage and the pH. Were 73% of the removal efficiency was seen at 90 min of the time, 85% at 1.8gms of the dosage and the pH was about 6 for removal of 93%. Langmuir isotherm, Freundlich isotherm and Temkin isotherms were also studied and the rate of adsorption obeys first order rate equation.

Key words: Fluoride, Adsorption, Kinetics,Isotherms.

I. INTRODUCTIONS

Water is one of the most important elements on earth. Every living being needs water for its survival, without water everything will perish. According to the UN estimates, the total amount of water on earth is about 14,000 billion cubic meters which is enough to cover the earth with a layer of 3,000 meters depth. However the fresh water constitutes a very small portion of this enormous quantity[(3).] About 2.7% of the total water available on earth is fresh water of which about 75.2% lies frozen. In Polar Regions and other 22.6% is present as ground water. As per the Government of Indian Publication (Ministry Of Water Resources, 2007) a basic necessity of industrial development is adequate availability of water. The increase in utilization of freshwater for industrial purposes are a serious problem faced all through the world[(3)]. Water is life for all living beings but nowadays pure water is available to very few people and most of the water is contaminated.

Fluoride is an extremely reactive member of the halogen group of element having atomic weight of 18.99 and atomic no is 9. It is the lightest halogen and 13th most prevalent element. Fluoride is a naturally occurring element in minerals, geo-chemical deposits and natural water systems and enters food chains through either drinking water or eating plants and cereals. Fluorine and its compounds are valuable and extensively used in industry such as fertilizers, production of high purity graphite, semiconductors, electrolysis of alumina, etc.

II. MATERIAL AND METHODOLOGY

Limestone is a sedimentary rock composed of mainly skeletal fragments of marine organisms such as coral, forams and mollusks. Its major materials are the minerals calcite and aragonite.Limewater is the common name for a saturated solution of calcium hydroxide. Lime Slurry is an odorless, low viscosity suspension of calcium hydroxide in water. The solubility of limestone in water and weak acid solutions leads to karst landscapes, in which water erodes the limestone over thousands to millions of years. Most cave systems are through limestone bedrock. Limestone has numerous uses: as white pigment or filler in products such as toothpaste or paints, as a chemical feedstock for the production of lime, as a soil conditioner, or as a popular decorative addition to rock gardens. Helps makes lawns green.Building materials: Is an essential component in concrete.Decorative floor covering: Travertine tile is a form of banded limestone.

a. ANALYSIS OF PHYSICO-CHEMICAL CHARACTERISTICS OF DRIED SLURRY POWDER

It‘s very important to analyze few physicochemical characteristics of the material like moisture content, specific gravity, decolorizing power, pH, color, surface area and bulk density as shown in the table-1 below,

TableNo-1

Sl/no	Physo-chemical characteristics	Obtained Results	Units
1	MOISTURE CONTENT	0.8	%
2	pH VALUE	8.2	------
3	SPECIFIC GRAVITY	2.5	-------
4	BULK DENSITY	1.205	g/cm^3
5	COLOR	white	------
6	SURFACE AREA	505.84	m^2/g

b. METHODS

There are several methods for removal of fluoride referred from the standard methods is as follows

1) Preliminary distillation step
2) Ion-selective electrode method
3) SPANDS method
4) Complex one method
5) Ion-selective electrode flow injection analysis.

From this above methods, SPANDS method is used of removal of fluoride.

Batch Sorption Process

In batch sorption, a pre-determined amount of adsorbent is mixed with the sample, stirred for a certain time and subsequently separated by filtration. Powder adsorbent is more suitable for the batch type contact process.

- Determination of adsorbing capacity polishing slurry on adsorption as a function of,
- Selection of optimum contact time
- Determination of Optimum Dosage
- Effect of pH of Fluoride Removal

Selection of optimum contact time: In this experiment for the study of effect of contact time 100ml of 5 mg/L fluoride solution was mixed with 1gm of the slurry powder and stirred for different time period of contact time and time intervals varies as 10, 20, 30, 40, 50, 60……100 minutes. This is filtered and analyzed for fluoride concentration using spectrophotometer method.

Selection of optimum dosage: To determine the optimum dosage of adsorbent, adsorbents were added to the conical flask containing known concentration of fluoride solution (5 mg/L). The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies from 0.2, 0.4, 0.6……..2.2 grams. Filtered and analyzed for residual and removal of fluoride concentration.

Determination of optimum pH: To determine the optimum ph, series of conical flask were taken with 100ml of 5 mg/L of fluoride solution. Optimum dosage of slurry powder (1800mg/100ml) is added. The pHs of the flasks were adjusted from 2 to 9. The flasks were shaken for optimum contact time.

Sorption equilibrium: In order to successively represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Three kinds of several isotherms equations were tested to fit the experimental data.

Langmuir equation: $C_e / q_e = (C_e / q_{max}) + [1/(q_{max} b)]$

Freundlich equation: $\log q_e = \log K_F + (1/n) \log C_e$

Temkin equation: $q_e = a + b \ln C_e$

Where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of metal ions in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, q_{max} (mg/g) is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on a sorbate surface, 'b' which reflects quantitatively the affinity between the adsorbent and adsorbate. Freundlich treatment gives the parameters, n, indicative of bond energies between metal ion and the adsorbent and KF, related to bond strength.

III. RESULTS

This chapter shows the results obtained from use of the stone polishing slurry powder

1. Effect of Contact Time
2. Effect of Dosage
3. Effect of Ph
4. Sorption Kinetics
5. Sorption Equilibrium

Batch Sorption experiments

1. **Effect of Contact Time:** In this the optimum contact time of the material is consider which is obtained by considering different contact time for the material of a fixed weight. The time which shows more adsorption percentage is consider and taken as optimum contact time. In this study the optimum contact is found to be 90 minutes for the weight of 1gm. On further increases in dosage the adsorption decreases. The fig(1) shows the optimum time obtained.

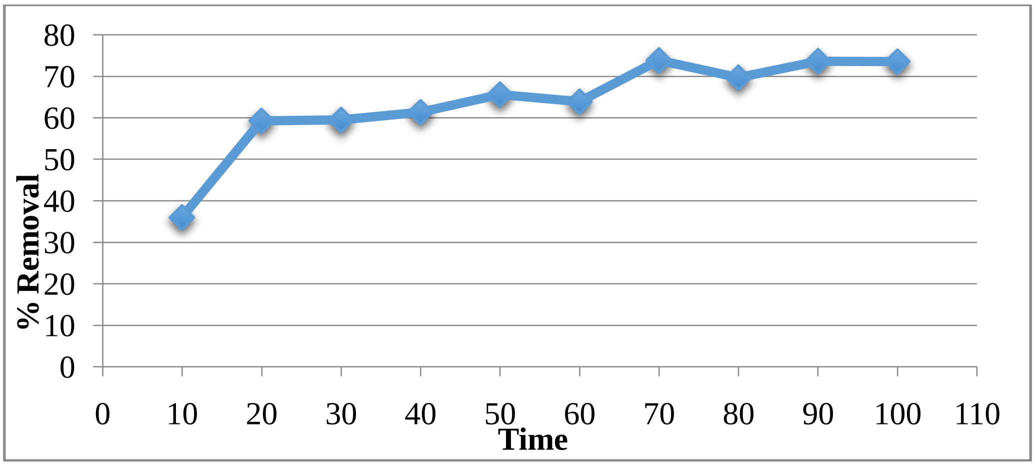

Fig.no-1Effect of Contact Time

2. **Effect of optimum dosage:** In this the optimum dosage of the material is consider which is obtained by considering different dosage for the material of a fixed time. The dosage which shows more adsorption percentage is consider and taken as optimum dosage. In this study the optimum dosage is found to be 1.8gm for the time of 90 minutes. On further increases in dosage the adsorption decreases. The fig (2) shows the optimum dosage obtained.

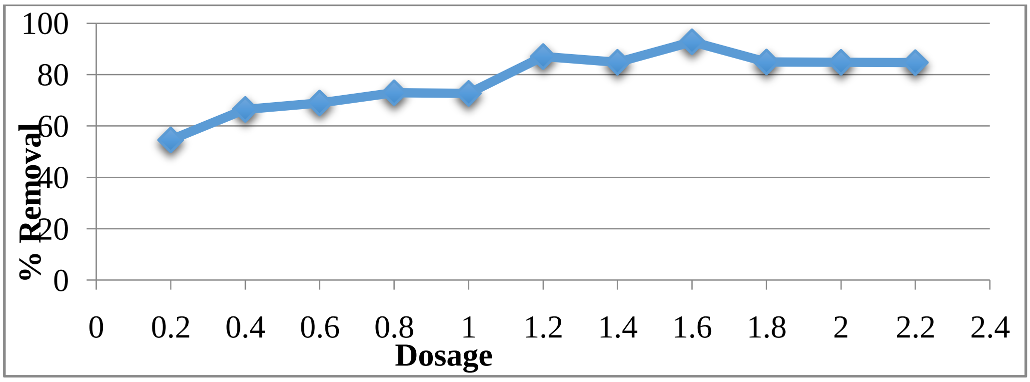

Fig.no-2 Effect of Dosage

3. **Effect of optimum pH:** In this the optimum pH of the material is consider which is obtained by considering different pH for the material of a fixed time and fixed dosage. The pH which shows more adsorption percentage is consider and taken as optimum pH. In this study the optimum pH is found to be 6 for the time of 90 minutes and dosage of 1.8gm. On further increases in dosage the adsorption decreases. The fig (3) shows the optimum pH obtained

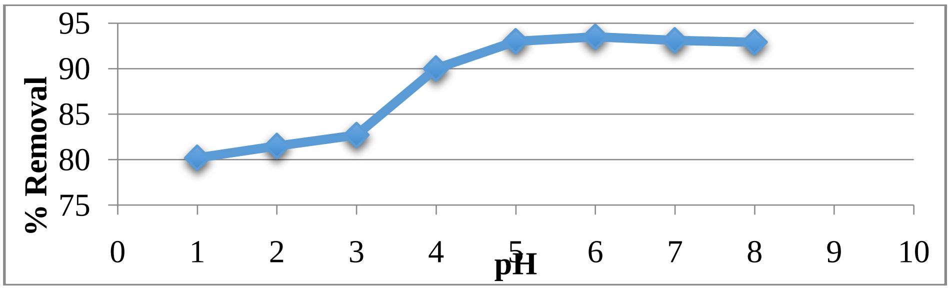

Fig.no-3 Effect of pH

Sorption kinetics

The kinetics of fluoride removal was performed at constant temperature at different time interval of adsorption. The batch kinetic data for the adsorption of the fluoride was tested for the first order reaction. The rate equation for the first order reaction is given by levenspiel,

Ln Ca/Co=K*T

$k=2.303/t \text{ X } \log_{10} a/(a-x)$

Where, a= Initial concentration of the fluoride, X= Amount of fluoride adsorbed at any time (t).,K= Rate constant., a-x= Residual amount of fluoride.This produces a straight line in graph with slope= k/2.303. From the value of graphical and calculated (K) values, it is observed that adsorption of fluoride follows first order rate equation. The value obtained from the graph (fig-3) and the calculated rate constant obey first order reaction.

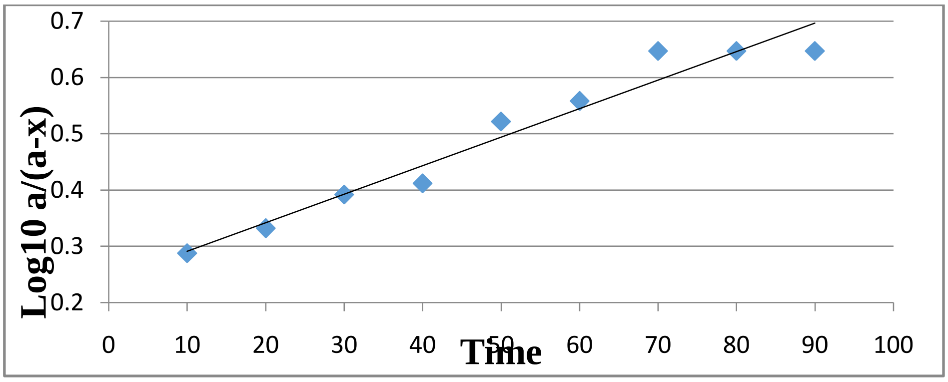

Fig.no-4 Reaction Rate Constant for Dry Stone Polishing Slurry

Sorption Equilibrium

Sorption equilibrium isotherms are used for the estimate of the amount of sorbate needed for sorbing a required amount of sorbate from solution. The most widely used equation to present the adsorption data are Freundlich, Langmuir and Temkin isotherm. The sorption equilibrium data are filled for all the three isotherms.

1. The Freundlich isotherm

The liner form of the Freundlich isotherm is

$X/M = K\,C^{1/n}$

$\log_{10} X/M = \log_{10} K + 1/n \log_{10} C$

Where, X/M= amount of sorbate adsorbed per unit weight of adsorbent at equilibrium.X= Amount of adsorbate removed (mg/L), C= Equilibrium concentration of adsorbate in solution, K= an empirical constant related to sorption capacity, n= an empirical constant related to sorption intensity.The plot of $\log_{10} \frac{X}{M}$ verses $\log_{10}$ C gives a straight line with slope 1/n and intercept=$\log_{10} K$, knowing slope and intercept "1/n" and "K" are calculated.

2. Langmuir's Isotherm

The Langmuir's Isotherm is used to describe the single layer adsorption and the linear form of the Langmuir's isotherm is

X/M= abc / (a + bc)

C / (X/M) = 1/ab +c/a

Where X/M = amount of adsorbate adsorbed per unit weight of adsorbent, C= Equilibrium Concentration of adsorbent in solution after adsorption or saturated concentration, "a" and "b" are empirical constants.

Plot C/(X/M) Verses C produces a straight line graph. The value of constants 1/b and 1/ab are calculated by intercept and slope. 1/ab = intercept, slope= 1/a.
The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless constant separate factor or equilibrium parameter which is defined by Webber as,R = 1 / [(1+a) C_o] where a= Langmuir Constant and Co= Initial Solute concentration (mg/l). The nature of the isotherms is indicated by the RL value as follows

RL value Type of isotherm
0 < RL<1 Favorable
RL >1 Unfavorable
RL =1 Linear
RL =0 Irreversible

3. Temkin isotherm

The simple form of adsorption isotherm model has been developed considering the chemisorptions of an adsorbate onto the adsorbent is represented as
X=a + b In C

Where C= Concentration of adsorbate in solution at equilibrium (mg/L).X= Amount of metal adsorbed per unit weight of adsorbent (mg/L). a= an empirical constant related to adsorption capacity. b= an empirical constant related to intensity of adsorption. The plot of in C vs X gives a straight line with slope and intercept knowing intercept and slope the constant a and b are calculated and the constant "a" and "b" are evaluated by least square analysis.

The following table-2 shows the results obtained from Freundlich, Langmuir and Temkin isotherm.The experiment studied on the Freundlich isotherms shows (n<1) n value is less than one and 1/n value is greater than one hence its dose not obey the Freundlich isotherm. The study conducted on Langmuir isotherm shows that R value is less than one (R<1) and obey the Langmuir's isotherm and it is also seen that the study obeys Temkin isotherm also

Table.no-2

Adsorbent	Freundlich Isotherm	Langmuir Isotherm	Temkin Isotherm
Dry Stone Polishing Slurry	Constant 1/n =1.344, K =0.0115	Constant a = 0.014, b =0.176, R =0.197 (0<R<1, Favorable)	Constant a =0.002, b =0.003

IV. CONCLUSIONS

Based on the experiment study following conclusions are drawn

1. The experiment is conducted on the removal of fluoride by Adsorption using stone polishing slurry powder as adsorbent where the removal efficiency of fluoride from synthetic solution is seen.
2. The kinetics of adsorption of fluoride with stone polishing slurry powder was studied by estimating the effect of contact time on the percentage (%) removal of fluoride. The data and results from the experiment used to removal of fluoride increases with increase in contact time and attain equilibrium at particular time. The optimum contact time for the stone polishing slurry powder is 90minutes with removal efficiency of 73%.
3. The experiment on optimization of dosage of adsorbent reveals that increase in amount of dosage added increases the removal of fluoride from the solution. Optimum dosage for the stone polishing slurry powder is 1.8grms with removal efficiency of 85%.
4. The adsorption of fluoride is mainly pH dependent. The removal efficiency of adsorbent increases with decrease in pH value. It has been observed that maximum adsorption takes place around pH 6 with removal efficiency of 93%.
5. The rate of adsorption of fluoride obeys first order rate reaction.
6. The result of the batch experiment follows Freundlich isotherm (1/n<1), Langmuir isotherm (R<1) and Temkin isotherm**.**

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