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Analysis, Mitigation and Defluoridation of Drinking Water

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ABSTRACT
Excess fluoride in drinking water is reported from more than 35 countries around the globe with India and China, being the worst affected. In countries like India, the severe contamination of drinking water with excess fluoride, acquired the dimensions of a socio-economic rather than a public health problem triggering defluoridation research .The objectives of the present work include preparation of various combinations of silica and calcium phosphate and use of these as potential adsorbents for defluoridation of drinking water. In order to study the effect of various factors like adsorbent dose, contact time and temperature on defluoridation of water using silica calcium phosphate in a series of batch sorption experiments were conducted. The obtained results were analyzed by Langmuir and Freundlich isotherms and it was found that defluoridation follows Langmuir adsorption isotherm.
Keywords: Fluorosis, fluoride, defluoridation, silica, calcium phosphate, adsorption, batch.

INTRODUCTION

Fluoride is a trace element; it occurs in tiny amounts or traces and plays a major role in health for even small portion of it can significantly affect health [1]. Excess fluoride in drinking water is reported from more than 35 countries around the globe with India and China, being the worst affected. In countries like India, the severe contamination of drinking water with excess fluoride, acquired the dimensions of a socio-economic rather than a public health problem triggering defluoridation research [2]. The World Health Organization has specified the tolerance limit of fluoride content of drinking water as 1.5 mg/L .One of the most important preventive measures of fluorosis is provision of drinking water containing fluoride within tolerance limits [3]. Endemic fluorosis resulting from high fluoride concentration in groundwater is a public health problem in India. The available data suggest that 15 States in India are endemic for fluorosis (fluoride level in Indian drinking water >1.5 mg/l), five of these have category III (>50% of the districts affected) [4]. World Health Organization (WHO) has set the upper limit of fluoride concentration in drinking water at 1.5 mg/l [5]. The Bureau of Indian Standards, has therefore, laid down Indian standards as 1.0 mg/l as maximum permissible limit of fluoride with further remarks as "lesser the better" [6]. Fluorosis is a diseases caused by an excess of fluoride in water. It has been estimated that 25-30 millions peoples are at a risk of developing fluorisis and half a million are suffering from it. Fluoride is retained in the bones and induces hardening of all the bones, including the spine hypertrophy of the joints and a bone is seen, similar to osteoarthritis. Sclerosis or ossifications of the posterior longitudinal ligament can occur with resulting mydopathy and radiculopathy from root comparison. The entire spine can by ossified with fluorisis [7].

People are consuming fluoride in water up to 18 mg/L. Fluoride being an electronegative element and having a negative charge is attracted by positively charged ions like calcium (Ca^{2+}). Bone and tooth having highest amount of calcium in the body attracts the maximum amount of fluoride. It is easily absorbed by the body from contaminated drinking water. After absorption, fluoride ion is quickly distributed throughout the body, easily crossing the membranes and going into tissues. It accumulates in body due to high reactivity of fluoride ion with calcium of teeth and bones. It forms calcium fluorophoshate (Fluorapatite) crystal and leaves unbound calcium in the same tissue, which gets calcified and in turn results in stiffness of tissues and joints. This finally leads to skeletal fluorosis in later stage. That's why fluoride is called as bone seeking mineral and bones are sink for fluoride. About 90% of the fluoride retrieved in body is associated with calcified tissues. and is deposited as Calcium Fluoroapatite crystals. Intake of fluoride above 1.5 mg/L may lead to serious manifestations[8].

Different techniques have been used to carry out water defluoridation: Membrane separation techniques have also been investigated for the effective separation of fluoride using electrodyalysis [9, 10] nanofiltration [11, 12], ion exchange membrane [13-16], chemical treatment [17-19] and adsorption into materials [20-22]. The adsorption process is a widely accepted pollution-removal technique, because of its ease of operation and cost-effectiveness. Different types of adsorbents such as natural, synthetic, and biomass, are used for removal of fluoride from water [23].

The objectives of the present work include-

1. Comparision of the adsorption capacity of adsorbents silica gel and calcium phosphate in varying proportions (1:1 and 1:2).
2. Batch sorption studies of these adsorbents to study their defluoridation capacity.
3. Batch sorption kinetic study of the data obtained by the sorption experiments.

MATERIALS AND METHODS

Silica Gel and Calcium Phosphate were obtained from Central Drug House, Pune (India). All the other reagents were of Analytical Grade. Double Distilled water was used throughout the experiments.

Preparation of Adsorbents

Inorganic materials often show good mechanical properties, high rigidity, thermal stability and resistance against microbial attack and organic solvents, which make them ideal supports for affinity separation. Therefore silica gel may be a better candidate for the following qualities: it is an amorphous inorganic polymer composed of siloxane groups (Si–O–Si) in the framework and silanol groups (Si–OH) on the surface which can be easily functionalized by chemical modification; moreover, it is biocompatible andbiologically inert [24]. Calcium phosphate with apatite structure ($Ca_{10}(PO_4)6(OH)_2$) is a sparingly soluble mineral with strong affinity for adsorption of radio nuclides and heavy metals. The use of calcium phosphate as an adsorbent is due to its large specific area, high thermal and chemical stability, high ionic exchange capacity and its stability towards ionizing radiation [25]. Keeping in view the properties of the above mentioned adsorbents, mixture of the two were used in varying proportions. Combination of Silica and calcium phosphate were narrowed down to two proportions 1:1 and 1:2 based upon their defluoridation capacity.

Batch Studies

In order to explore the effect of influencing factors such as pH, temperature, contact time, quantity of adsorbent and initial fluoride concentration, a series of batch adsorption experiments were conducted. Batch adsorption experiments were performed by agitating specified amount of adsorbent in a definite amount of fluoride solution. The reaction mixture was agitated at 200 rpm for an optimum period of time at room temperature on a mechanical shaker (Remi Equipments, Mumbai India). After equilibrium the aqueous phase concentration of fluoride was analyzed with fluoride sensitive electrode (510, Eutech Instruments, Mumbai, India).Percentage removal of fluoride was obtained using equation-

$$\% \text{ Removal} = C_i\text{-}C_e/ C_i \times 100 \quad (1)$$

The amount of fluoride adsorbed per unit mass of adsorbent q_e (ppm/g) was obtained using the equation-

$$q_e = (C_i - C_e) / m \times v \quad (2)$$

Where C_i and C_e denoted the initial and equilibrium fluoride ion concentration (mg/L) respectively, m is mass of adsorbents and v being the volume of fluoride solution.

Adsorption Isotherm Model

Both Langmuir's and Freundlich's adsorption isotherm equilibrium models were used for the analysis of the Silica-Calcium–fluoride sorption system.

Freundlich Isotherm

Freundlich adsorption isotherm model used to study the non-ideal adsorption involving heterogeneous adsorption phenomena was evaluated by the equation (3) where K_f and 1/n are empirical constants.

$$\text{Log } q_e = \log K_f + 1/n \log C_e \quad (3)$$

Langmuir Isotherm

The rearranged Langmuir's adsorption isotherm model for evaluating the monolayer sorption phenomena as depicted in equation (4) where q_e (mg/g) is the amount of metal ion sorbed by the adsorbent at the equilibrium, Q_o (mg/g) the maximum metal sorption, C_e (mg/L) the concentration of metal in solution at the equilibrium and b (L/mg) is the Langmuir adsorption equilibrium constant [26].

$$C_e/ q_e = 1/ Q_o b + C_e/ Q_o \quad (4)$$

RESULTS AND DISCUSSION

Batch Studies

Effect of Contact Time

Effect of contact time on the percentage removal of fluoride was studied at different initial fluoride concentrations by keeping other parameters constant. The effect of contact time on removal of fluoride and the equilibrium concentration values q_e for the different fluoride concentrations is shown in Figure-1 (a) and (b) and Figure-2 (a) and (b). It was observed that with the increase in contact time, the percentage removal of fluoride increases and then removal becomes stable. This is may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in decrease of overall percent removal.

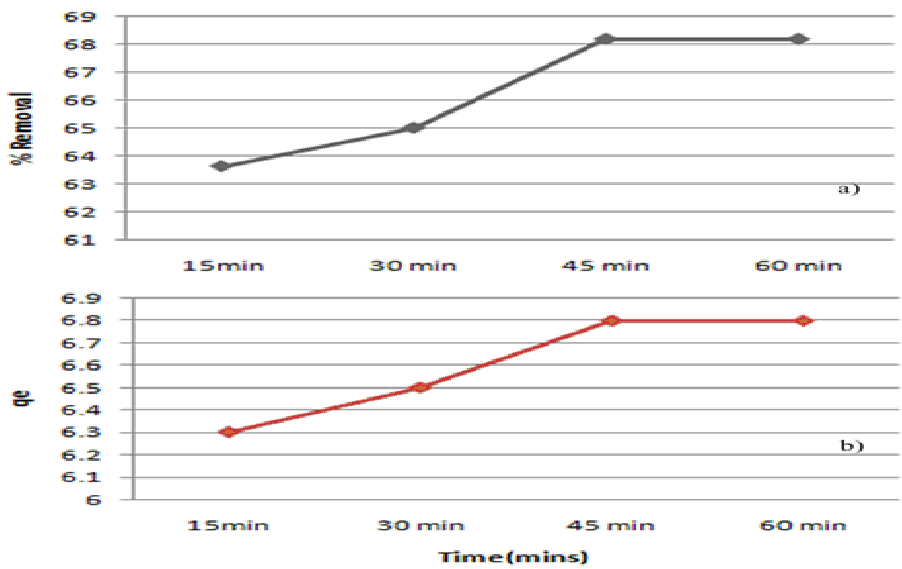

Fig.-1: Effect of contact time on (a) % removal (b) equilibrium concentration values of 1:1 Silica and Calcium Phosphate

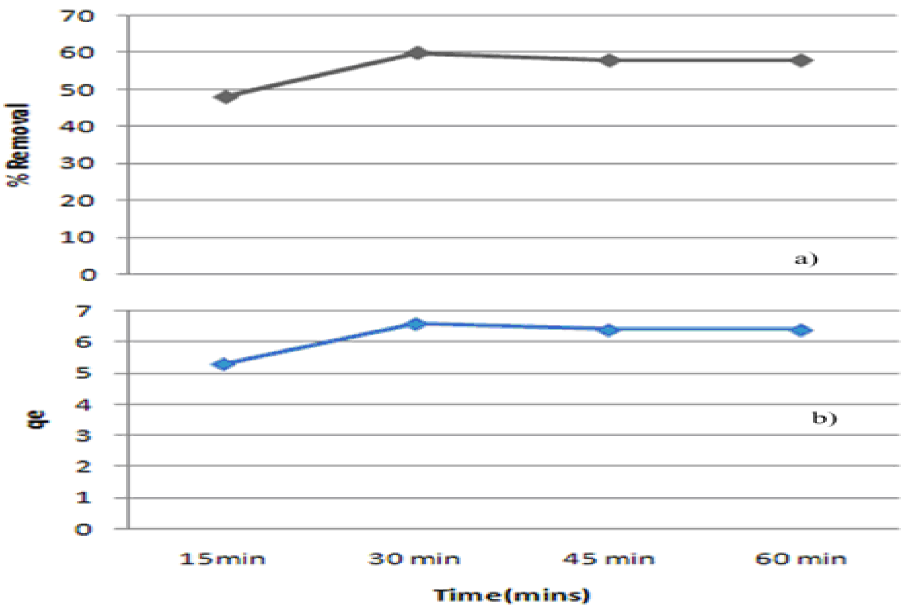

Fig.-2: Effect of contact time on (a) % removal (b) equilibrium concentration values of 1:2 Silica and Calcium Phosphate

Effect of Adsorbent Dose

The effect of adsorbent dose on fluoride removal at fixed initial fluoride concentration is shown in Figure-3 (a) and (b) and Figure-4 (a) and (b). It was observed that percentage removal of fluoride increased with the increase in adsorbent dose. This can be explained by the fact that greater the mass of the adsorbent, larger would be the contact surface offered for the adsorption.

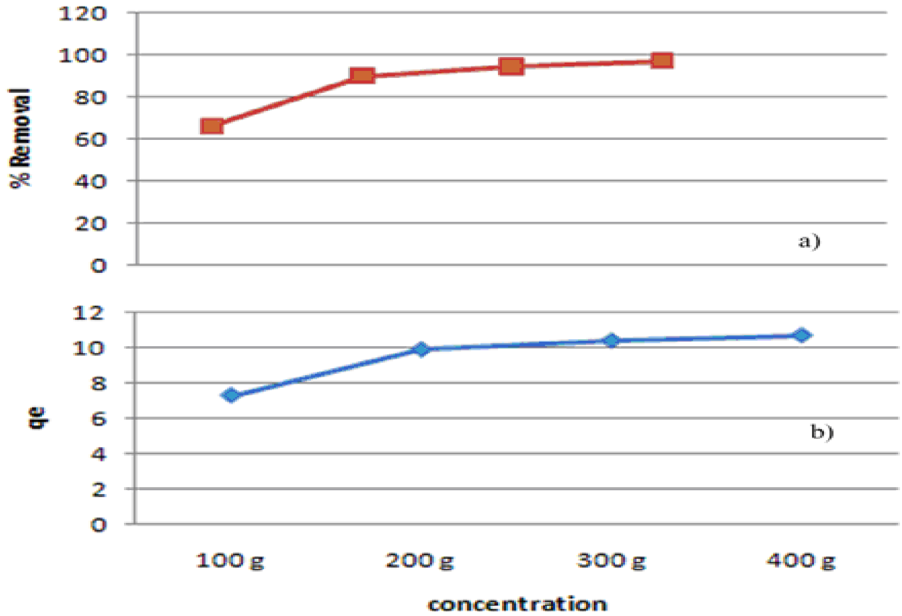

Fig.-3: Effect of concentration on (a) % removal (b) equilibrium concentration values of 1:1 Silica and Calcium Phosphate

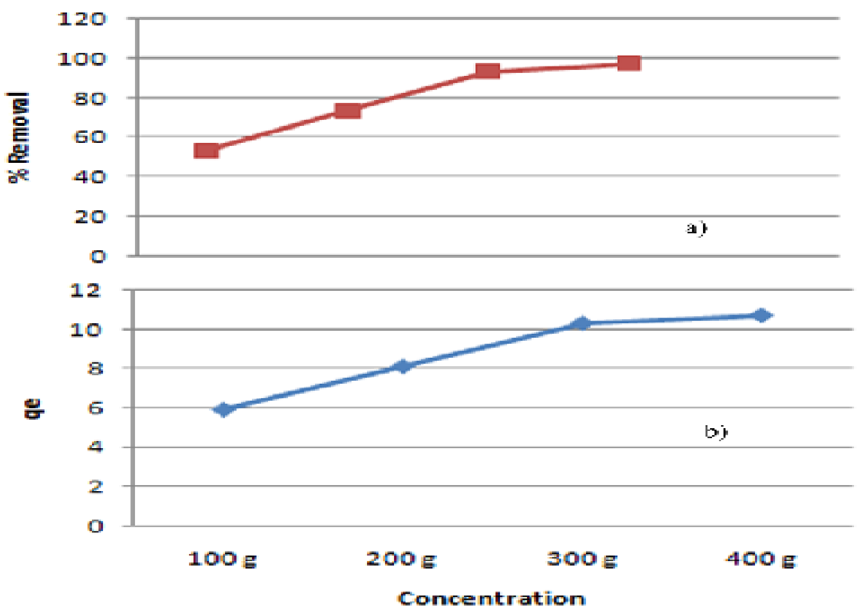

Fig.-4: Effect of concentration on (a) % removal (b) equilibrium concentration values of 1:2 Silica and Calcium Phosphate

Effect of Temperature

The temperature effect was carried out at 5°C, 25 °C and 50°C to study the influence of temperature on the defluoridation capacity of adsorbent silica and calcium phosphate (Figure-5 and 6 (a) and (b)) Studies show that adsorption and removal increases at higher temperature due to energy of activation gained by molecules which in turn increases removal.. These results show that decrease in temperature is unfavorable and increase in temperature is a favorable factor for defluoridation by silca calcium phosphate combination.

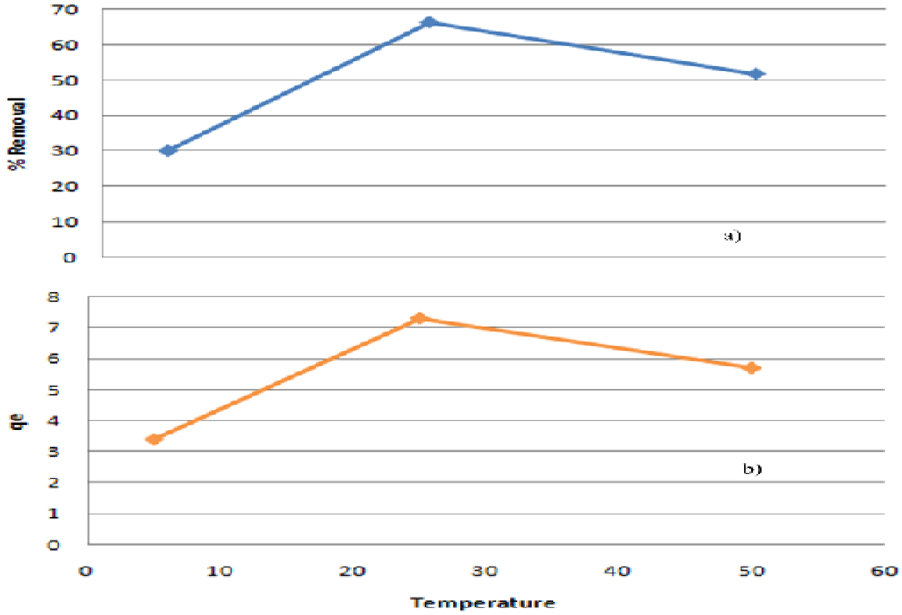

Fig.-5: Effect of Temperature on (a) % removal (b) equilibrium concentration values of 1:1 Silica and Calcium Phosphate

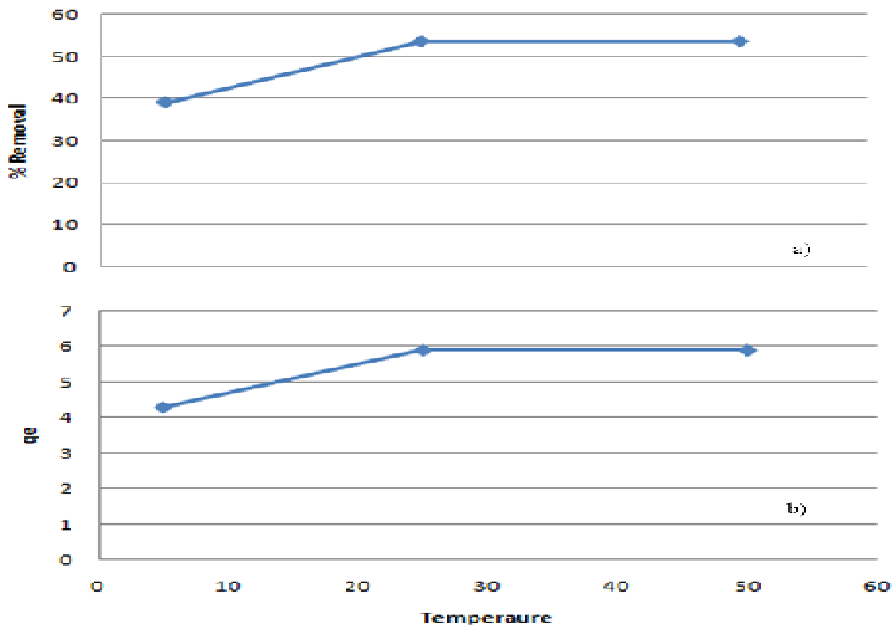

Fig.-6: Effect of Temperature on (a) % removal (b) equilibrium concentration values of 1:2 Silica and Calcium Phosphate

Sorption Kinetics

Adsorption isotherm

Figure 7(b) and 8 (b) shows the linear plots of log q_e vs log C_e indicating Freundlich adsorption model for 1:1 and 1:2 and the linear plots of C_e Vs q_e in Figure-7 (a) and 8 (a) shows the Langmuir adsorption isotherm for 1:1 and 1:2 silica calcium phosphate respectively. The value of regression coefficient for Langmuir isotherm is 0.997 and 0.976 for 1:1 and 1:2 combinations. The two values of regression coefficient show that defluoridation by 1:1 silica calcium phosphate combination follows the Langmuir isotherm better than 1:2 combination.

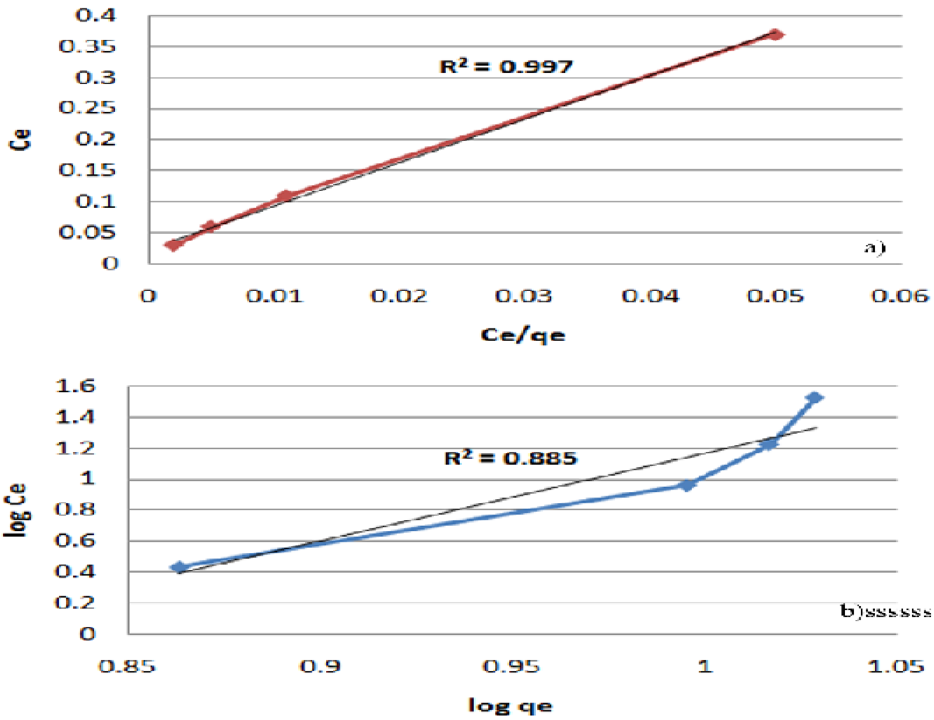

Fig.-7: (a) Langmuir Isotherm (b) Freundlich Isotherm for 1:1 Silica and Calcium phosphate

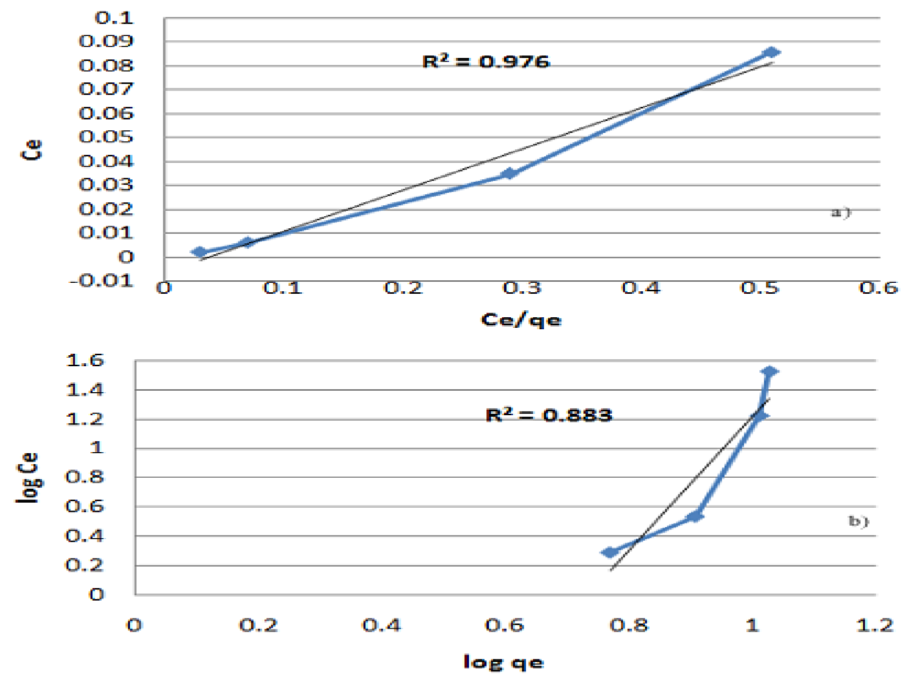

Fig.-8: (a) Langmuir Isotherm (b) Freundlich Isotherm for 1:2 Silica and Calcium phosphate

CONCLUSIONS

Removal of fluoride ions from aqueous solution by silica and calcium phosphate was investigated through batch studies and the following conclusions were obtained.

(1.) The combination of Silica and Calcium Phosphate is quite efficient as it is capable of removing nearly 100% of fluoride from water. There are two main reasons for using this combination-

a. Calcium ions present in Calcium Phosphate have a very strong affinity for Fluoride ions. This is the reason for effective removal of Fluoride from water. Same mechanism takes place in human body. The fluoride ingested through Fluoride contaminated water or other sources affect the teeth or bones. Since both of them have Calcium present in a large amount naturally the teeth and bones serve as sinks for Fluoride accumulation. Thus ingestion of excessive fluoride over a period of time causes Dental and Skeletal Fluorosis.
b. Another reason is that Calcium Phosphate and Silica do not leave any harmful residues in water after adsorption. Thus water after adsorption is safer to drink compared to other defluoridated water samples.

(2.) Also the two adsorbents Silica and Calcium Phosphate are cheap and easily available. The whole defluoridation unit would not cost more than Five hundred Rupees. Thus it is within the reach of the common man.
(3.) The combination of silica and calcium phosphate in 1:1 combination is a better adsorbent than 1:2 combinations.

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