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Kinetic Studies for the Removal of Fluoride from Water by Adsorbents Prepared from Biowaste Materials

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Abstract: ***Activated carbons prepared from biomaterial like 'Typha Angustata' (TAC), 'Lagenaria Siceraria' (LSSC), 'Acacia Farnesiana' (AFC) as adsorbents. Adsorption of fluoride using these activated carbons studied by batch adsorption method. Kinetics of adsorption has been explored by analyzing the data using various kinetic model equations such as first order, pseudo first order, modified pseudo first order, second order, pseudo second order, intra particle diffusion model and pore diffusion models kinetic parameters viz, rate constant and correlation coefficient for each kinetic equation were calculate and discussed. Thermodynamic studies have also been made in this investigation.***

Keywords: Batch Adsorption, New activated carbons and kinetic studies.

1. Introduction

The adsorption process. In view of the harmful effects caused by taking excess fluoride through drinking water, it is essential to develop a suitable method to decrease its level below the permissible limit. The methods of defluoridation recommended so far are aimed at bringing the fluoride levels to the WHO standards (0.5-1.5 mg/L). Most of the commercial activated carbons are either coal-based. The long-term availability of coal, environmental impacts and the potentially increasing cost has encouraged researchers to find other alternatives, which may be cost effective and equally potential. The demand for activated carbon is increasing owing to the increase in the utility of the carbon materials in pollution control. As a result, the cost of activated carbon is also growing depending on the application. Designing ways for the production of activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon-rich and low ash precursors and sources are being explored for the production of carbon materials. The main purpose of this work is to study the removal of F^- ion from potable waters by adsorption technique in batch process. This fluoride ion removal research has several aims to achieve its desired output, and the following objectives have been undertaken:To study the removal of fluoride ion from potable water using activated carbon adsorbents prepared from low cost-bio adsorbents. To establish the adsorption isotherms of the activated carbon adsorbents with respect to various physicochemical parameters. To study the kinetics and thermodynamics ofTo compare the performance of adsorbents probed for removal of fluoride ion. To evaluation of the field application by taking high fluoride ion concentration water from one of the selective revenue sub divisions.

2. MATERIALS

Acacia farnesiana (AFC, Typha angustata (TAC)) and Lagenaria siceraria shell carbon (LSSC)

3. METHODOLOGY

3.1 Carbon Preparation

Dry fruits were collected in bulk and washed in cold water to remove dust on fruit.Dried in sunlight about one week and cut into small pieces carbonized in muffle furnace (in absence of air) about 7 hours at 700°C. After carbonization carbon was poured in a fluoride free water (Double distilled water) filtered and washed in several times with cold fluoride free water and dried in an air oven at 110°C carbon was sieved into desired particle sizes Powder form in individual was taken in a one liter volumetric flask (about 50g) and mixed with approximately 700-800 ml 0.1M solution HNO_3 and boiled for 2 to 3 hours on flame (Liquid phase oxidation). After acid treatment they were filtered and washed with hot water with several times (until the effluent pH was retained i.e. 6.80) to remove un-reacted acid on carbon surface. After liquid phase oxidation each carbon was sieved into a particle size in the range of 40-120 mesh sizes.

3.2 Characterization of Activated carbons

XPS,FT-IR,XRD,SEM-EDXBETTGA-DTA etc., ORION F^- ion selective electrode.

4. Experimental

100 ml of standard fluoride solution (5 mg/L) is pipette out into a 500 ml beaker. 0.5 g/L of one of the prepared carbons is added and is stirred at 200 rpm mechanically for 30 minutes. The solution is filtered through Whatman No-42 filter paper. The fluoride concentration in the sample after defluoridation is determined with electrode with ORION ion selective and prepared standard curve. The same procedure has been adopted for the experiments carried out by varying (i) adsorbent type (TAC, LSSC, AFC) (ii) effect of particle size (45 microns to 250 microns) (iii) initial pH of the standard fluoride solution (ranging from 3 to 10), (iv) agitation time (ranging from 5 – 70 min), (v) dose of adsorbent (ranging from 0.5 to 7.0 g/L and (vi) initial concentration of the standard fluoride solution (ranging from 1.5 to 15 mg/L), vii) by changing the solution temperature (283-313K).

Using the following relationships:

Percentage removal ……………

$$(\%R) = \frac{C_{i-}C_e}{C_i} \times 100$$

Amount adsorbed (qe)……………… The percentage removal of F- ion and amount adsorbed (in mg/g) were calculated …. (qe) $= \frac{(C_i - C_e)}{m}$

Where Ci and Ce are the initial and final concentrations (in mg/L) of F- ion respectively and m is the mass of carbon (in mg/L). Blanks containing no F- ions were used for each series of experiments as controls. The average values of duplicate runs were obtained and analyzed. Error in data: ±1– 2% for percentage removal, ± 0.005–0.01 mg/g for amount adsorbed.

5. Results And Discussions

In the present work, Active Carbons derived TAC, LSSC and AFC have been explored for their sorption nature towards the Fluoride ion in effecting the defluoridation of water.In order to study the thermodynamic parameters, adsorption experiments have also been carriedout at different temperatures 298-318 K, and it has been noted that the adsorption process is exothermic in nature. For the active carbons TAC, LSSC and AFC, the optimum adsorbent dosages are found to be 3.5, 4.0 and 4.5 g /l and optimum time 35, 40 and 45 minutes respectively. At neutral pH, at room temperature 303 K and at 5.0 mg/l initial concentration, the fluoride removal capacity of these adsorbents is 96.80%, 92.80% and 90.00% for TAC, LSSC and AFC respectively. These active carbons have been found to be pH-sensitive and have shown good adsorption abilities towards Fluoride ion in the optimum pH range 6-7. In the study of effect of temperature on adsorption process, it is observed that percent removal decreases with increase of temperature.The fluoride loaded carbons can be regenerated with 10% NaOH solution but regenerated carbons show poor efficiency in further defluoridation process. However, as these adsorbents are prepared from bio-waste materials, regeneration may not be a vital option.Adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of fluoride onto carbon and also the homogeneous distribution of active sites on the adsorbent, since the Langmuir equation assumes that the surface is homogeneous. Further R^2 value of (TAC, LSSC and AFC) Langmuir Adsorption isotherm (Type-1) higher than the Freundlich Value, Temkin and D-R isotherm. In the Dubinin-Radushkevich Isotherm, the value of correlation coefficient is higher than Temkin value but lower than Langmuir values for all the three sorbents.Weber and Morris plots (Intraparticle diffusion plots) have been observed in separate stages; first linear portion (stage1) and second curved path followed by a plateau (stage2) in stage1, nearly 50% of fluoride is rapidly up taken by carbon adsorbents with in five minutes. This is attributed to the immediate utilization of the most readily available adsorbing sides on the adsorbent surfaces. In stage 2, very slowly diffusion of adsorbate from surface site into the inner pores is absorbed. Thus initial portion of fluoride adsorption may be governed by the initial intraparticle transport of fluoride controlled by surface diffusion process and later it is controlled by pore diffusion. The Bangham's plot (Pore diffusion plots) has been found to be linear for each adsorbent with good correlation co-efficient (>0.9) indicating that kinetics may be confirmed to Bangham's equation and therefore the adsorption of fluoride onto TAC, LSSC and AFC may be pore diffusion controlled. In Elovich plots high R^2 values suggests that diffusion accounted for the Elovich kinetics pattern conformation to this equation alone might be taken as evidence that the rate-determining step is diffusion in nature and that this equation should apply at conditions where rate desorption can be neglected. The fitting of the kinetic data demonstrates that the dynamics of sorption can be better described by pseudo second-order model indicating a chemisorptive rate limiting for all the three adsorbents, TAC, LSSC and AFC. We found that the optimum experimental conditions for the three developed AC's: TAC, LSSC and AFC at room temperature 30 $\underline{+}$ 1^0C are respectively: 35, 40 and 45 minutes as contact time; 3.5, 4.0 and 4.5 g/l as dose of the absorbent; and 6 to 7 as pH.

Among the three low-cost adsorbents under consideration, TAC possesses the highest or the maximum adsorption capacity. Hence it is the best and the most effective adsorbent in the removal of the dreaded fluoride content in water. The next in order on the basis of its efficacy in removing the Fluoride content is LSSC; AFC is also not far behind the first two in aspects of adsorption capacity and efficiency.

To know the defluoridation capacity of the prepared carbons with real samples, the researcher selected one revenue subdivision from a well-known fluoride effected areas in Prakasam district (A.P.-India) i.e. Kandukur sub-division which is comprising of 24 villages. 48 water samples have been collected from bore wells and hand pumps of these villages. Fluoride monitoring has been done along with various other parameters in ground water analysis. Almost all samples have fluoride concentration above permissible level. Various other ion concentrations are also observed beyond the permissible levels. With the adsorbents developed in this work viz., TAC, LSSC and AFC the percent removal of

Fluoride from the water samples have been found to be on average 85 %, 80 % and 75 % (on average) respectively of the original content of the fluoride in the water samples at optimum extraction conditions .

6. Conclusions

Batch adsorption experiments have been carried out for the removal of fluoride from its aqueous solution using the said sorbents. The adsorption of fluoride ion by AC's has been investigated as a function of pH, contact time (agitation time), initial F^- ion concentration, adsorbent concentrations (dose), adsorbent size (Particle size) and temperature. The results of the experiments have shown that the percentage of fluoride removal has increased with the increase of contact time and dose of adsorbent. On the contrary, the percentage of removal has decreased with the increase in initial concentration of the standard fluoride solution.

I conclude this chapter on an optimistic note that the findings in this work will be of immense use in the defluoridation of waters in rendering them potable especially in the fields where human suffering from fluorosis is prevalent. The methodologies developed in this work using the three active carbons viz., TAC, LSSC and AFC , derived from abundantly available low cost bio-materials are simple, effective, eco-friendly and economical and moreover, these procedures are easy to operate even at household levels even by un-skilled persons.

7. Suggestions

The suggested AC'S are very cheap and are abundantly available. Because of their economic viability, these low-cost adsorbents seem to have a rosy path in the process of eliminating the undesirable and unwanted ingredient, Fluoride, in waters. We claim that the active carbons developed in this work have been effective in the deflouridation of ground waters and this fact is reflected in the good positive correlations observed between vital parameters in correlation analysis. The high values of fluoride in the studied area are attributed to dissolution of fluoride from fluoride minerals which are found in abundance this area.

8. Scope of the Further Research

I hope and wish that my finding in this aspect of pollution control may evoke interest in the researchers in exploring the natural surface abilities of bio-sorbents in devising more simple and effective methodologies in controlling the dreaded fluorosis. Our entire research program is aimed to develop small scale process at house hold level, and then there is a chance to adopt the same process to large scale defluoridation methods suitable to municipal waters.

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