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Treatment of Groundwater by Defluoridation

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Abstract : Fluoride is a toxin that gets collected in bones and teeth of humans. It is also a cause of cancer in young individuals; osteoporosis; reduced mental growth; and hip fractures in the old people. Fluoride occurs in mineral deposits and infects our ground water resources. Along with subsurface waters, surface water supplies are also being polluted by the fluoride. Hence since long time many techniques have been devised to remove fluoride from the drinking water such as Precipitation, Ion exchange, Adsorption etc. In all of the devised techniques, adsorption is the most effective technique used at the present time. To prevent more costly techniques and materials, many adsorbents have been prepared from the waste materials which adsorb fluoride ions onto their surface. In this study, the adsorption potential of bagasse powder has been studied in order to consider its usefulness for removal of fluoride content from the water. Laboratory examination of the effectiveness of bagasse powder to remove fluoride from aqueous solution has been investigated and also the effect of various parameters such as pH, Temperature, Adsorbent dose and Contact time on the efficiency of the fluoride removal has been studied. The equilibrium data have been analyzed by the Freundlich and Langmuir adsorption models.
Keywords : Adsorption, Bagasse powder, Batch Adsorption, Defluoridation, Fluoride.

1. Introduction

Fluoride is necessary in small amount for the proper functioning and maintenance of the teeth and bones. Deficient amount of fluoride in the body leads to the dental cavities and weak bones. Fluoride enters the ecosystem through the natural phenomenon such as weathering of minerals and rocks having fluoride and anthropogenic activities such as industrial activities like discharges from the industrial establishments. In India, especially rural people are highly affected by the problem of fluorosis because they have groundwater as their

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major source of drinking water. Seventeen states in our country India are facing the problem of fluorosis.The conventional fluoride removal techniques such as Nalgonda technique, Ion-exchange, Reverse osmosis, Precipitation etc. have been widely used in the defluoridation of water. Ion exchange and reverse osmosis are cheap to conduct. Also,Nalgonda technique have also been very widely used in the villages and rural areas to remove fluoride from the groundwater which involves the addition of aluminium salts in the water.Besides all the methods used, adsorption is the most widely used method for the fluoride removal from the water due to less costly and easiness of the operation (Waghmare and Arfin, 2015).Many adsorbents have been used such as natural soil, termite mound, pineapple peel powder, lemon peel powder, rice husk, tamarind seed etc. have been successfully used to remove fluoride content from water. In the present researchBagasse Powder is usedfor the removal of fluoride from the groundwater.Sugarcane bagasse is the fiber that is left over after the sugars have been removed (Chakrabart et. al. 2016, Gandhi et. al. 2012).

2. Effects of Fluoride

Very high fluoride concentrations in the potable water badly influence the well-being of the water consumers and lead to fluorosis which occurs in three forms such as:

2.1 Dental fluorosis:

Dental fluorosis causes discoloring, mottling and blackening of the teeth. Children below 8 years of age are more susceptible to the dental fluorosis problems. If the fluoride level falls below 0.7 mg/l and the continuous exposure to such conditions is not prevented, then cavities begin to develop in the teeth along with several tooth deformities (WHO, 2004)

2.2 Skeletal fluorosis:

Skeletal fluorosis is the stage of bone deformities in which bones of the humans are deformed permanently along with pain in the muscles and other joints. Fluoride is a calcium loving element. When it reaches in the body through the groundwater ingestion, then it accumulates in the bones and thus weakens the bone structure (Jamode et al, 2004).

2.3 Non-skeletal fluorosis:

It causes the gastro problems along with neurological disorders. It also affects the I.Q. of the children. The mental growth of the children is retarded and increase in the nervousness, thirst etc. is noticed after fluorosis is detected in the body. It commonly affects the joints of the body and certain stomach and liver problems (Wondwossen, 2004).

3. Materials and Methods

3.1 Preparation of adsorbate solution

Dry 3-5 grams of AR grade sodium fluoride (NaF), (compound molecular weight is 41.99 and purity is 97 per cent) at a constant weight in a 110 ° C oven and cool in a desiccator. Weigh 2.2105 g of the NaF and transfer it quantitatively to a volumetric flask of 1000 ml. Dissolve with distilled water, and dilute to volume. Mix and transfer them for storage to a polyethylene bottle. Label as 1000 ppm Fluoride Stock Solution in distilled water. For a 100 ppm fluoride solution, dissolve 0.2210 g NaF and for a 10 ppm fluoride solution, dissolve 0.0221 g of NaF in the same quantity of the distilled water to prepare the desired stock solution (Bhaumik et al. 2011, Bhaumik et al. 2012, Bhaumik et al. 2014).

3.2Preparation of adsorbent

Bagasse powder was obtained from the sugarcane mill in directly powdered form. The bagasse powder was sieved through IS sieves of 150 μm and 300 μm size and the material passing through 150 μm and retained on 300 μm which has a geometricmean size is in the range of 150-300 microns was used in the test.

3.3 Calibration of Metrohm 692 pH/Ion Meter

A series of eight fluoride standards (ranging from 0.02 mg/l to 1 mg/l) were prepared using NaF in distilled water. Also, Total Ionic Strength Adjustment Buffer II (TISAB II) was prepared bymixing 4 gm of CDTA (trans-1, 2-diaminocyclohexane N, N, N´, N´-tetra acetic acid), 57 ml acetic acid and 58 gm of NaCl in 500 ml of distilled water keeping the pH between 5 and 5.5.The Metrohm ion meter was standardized and calibrated by this 8 fluoride standards.

3.4 Methodology

A stock solution with NaF salt is prepared which will be used further in the experimental study.0.221g NaF salt is added to 1000ml distilled water to prepare 100ppm stock solution of fluoride andit is kept in a plastic bottle for subsequent use. Further 100 ppm stock solution is diluted to 5 ppm for the study in the experiment. All the experiments were conducted at room temperature (29±2 degree Celsius) except where effect of temperature variation is to study on the fluoride sorption.100 ml of this test solution is taken in a 250 ml conical flask and adsorbent (bagasse) is added to the flask (Suman Mann,2014).The conical flask containing the test solution and the adsorbent is kept in a horizontal shaker for the study of the adsorption of fluoride by bagasse and also to study the effect of the different parameters such as pH, contacttime, Adsorbentdose, Temperature and initial fluoride concentration on the adsorption efficiency. After the required contact time, the sample is left for about 5 minutes to let the adsorbent settle and then the test solution is filtered. Final fluoride concentration is determined using Metrohm ion meter with ion selective electrode using Total Ionic Strength Adjustment Buffer II (TISAB II) to maintain pH and nullify the effect of the interference due to complexing ions. Batch study experiments were used to determine the effect of the different parameters on the removal efficiency.

Figure 1.Metrohm Ion meter

4. Results and Discussion

4.1 Effect of dose

The effect of the different adsorbent dose was studied by varying the dose of the adsorbent at constant pH of 7, and contact time of 120 minutes. From the study it was found that as the dose of the adsorbent is increased, the fluoride removal increased due to the availability of the increased active sites for the adsorption but after dose of 1.2g/100ml, the adsorption became more or less constant and after 1.4g/100ml, the adsorption efficiency started decreasing due to the non-availability of the active sites and site overlapping.

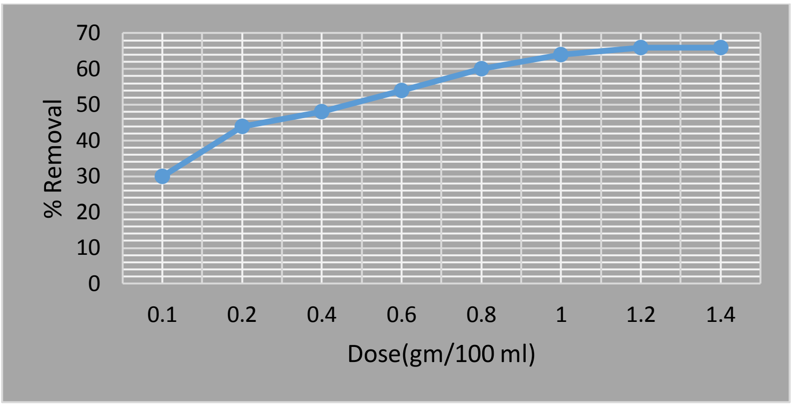

Figure 2. Effect of adsorbent dose on fluoride removal, Fluoride initial concentration is 5mg/L, pH is 7 and contact time is 120 minutes

4.2 Effect of contact time

The effect of contact time in this study was examined by changing contact time from 10 to 80 minutes at pH of 7 and dose of 1.2gm/100ml. The value of removal of fluoride increases with increase in contact time and it becomes constant after contact period of 50 minutes at pH 7.As the contact time is increased, the fluoride adsorption increased, but after some time it starts falling and attains a constant value at 50 minutes from the starting. The reason behind this may be attributed to the fact that the active sites on the adsorbent are fully occupied at this time and hence fluoride sorption becomes constant.

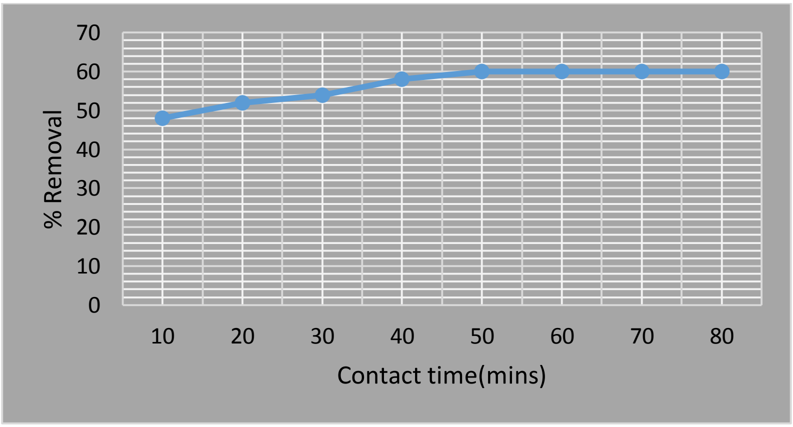

Figure 3. Effect of Contact time on fluoride removal, Fluoride initial concentration is 5 mg/L, dose is 1.2 g/100mL and pH is 7

4.3 Effect of pH

pH variation will be from 3 to 10 and its effect on the fluoride sorption will be studied. For the effective removal of the negatively charged fluoride ions, presence of positive hydrogen ions for the hydrogen bond formation must be favoring the absorbance of the fluoride anions on the surface of the adsorbent. Other parameters were kept constant such as adsorbent dose was kept at 1.2gm/100ml, contact time was kept as 50 minutes and temperature was maintained at room temperature. It isfound that fluoride removaldecreases with increasing pH up to 7 but from 8, there is sudden fall in the removal percentage. The reason behind this is attributed to presence of positive hydrogen ions which react with negative fluoride ions in the acidic rangeto form the hydrogen bond with the fluoride ions of the test sample. The hydroxyl ions neutralize the functional groups in the basic medium and decrease the adsorption due to repulsive forces. Hence the optimum pH for the maximum adsorption of fluoride from the water is ‘7’.The adsorption is maximum in the pH range of 3-6.

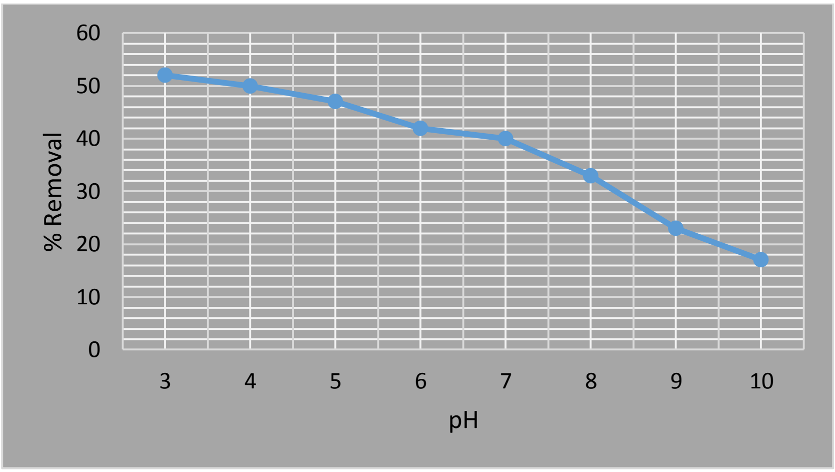

Figure 4.Effect of pH on sorption of fluoride, Fluoride initial concentration is 5 mg/L, dose is 1.2 g/100mL and contact time is 50 mins.

4.4Effect of initial fluoride concentration

Keeping all other parameters constant, the initial fluoride concentration is varied in the range of 2.5 g/l and the removal efficiency is studied. It was found that with the increase in the initial fluoride concentration, the removal efficiency decreased since the active sites on the adsorbent are limited and can adsorb limited fluoride ions. Hence sites become saturatedand cannot adsorb further additional fluoride ions up to 12.5 mg/l, the decrease is visible after which the efficiency becomes more or less constant.

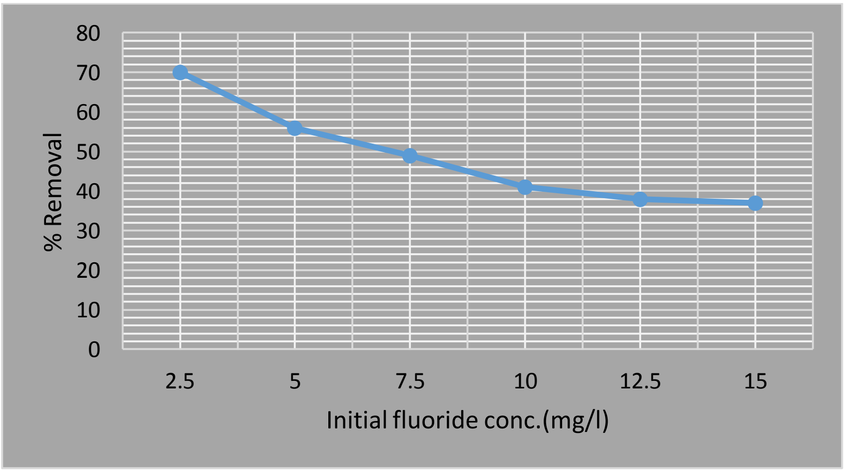

Figure 5. Effect of initial fluoride concentration of fluoride sorption (Adsorbent dose is constant)

5. Adsorption Isotherms

Adsorption isotherms are the curves plotted between amount of solute adsorbed per unit mass of adsorbent (q_e) and concentration of solute in the solution at equilibrium (C_e)at any particular temperature. There are two types of isotherms which are used to study the mechanism of adsorption on any surface such as Langmuir and Freundlich isotherms. The data of adsorption obtained from tests was fitted on Langmuir and Freundlich isotherms to find the suitable adsorption mechanism.

5.1Langmuir isotherms

Langmuir model assumes that a saturated layer of solute molecules on the adsorbent surface enhances theadsorption and maximum adsorption is achieved in that case. It also assumes that adsorption energy is constant and adsorbate molecules do not migrate or move in the planar surface.(Partha.S.Ghosal, 2017)**.**

Table 1. Adsorption data for plotting Langmuir and Freundlich isotherms

Fluoride Initial conc. (Co)	Fluoride Final conc.(Ce)	Dose	Fluoride removed	q_e(mg/g)	$1/q_e$	$1/C_e$	Log q_e	Log C_e
5	3.50	0.1	1.50	1.500	0.666	0.286	0.176	0.544
5	2.80	0.2	2.20	1.100	0.909	0.357	0.041	0.447
5	2.60	0.4	2.40	0.600	1.667	0.385	-0.222	0.415
5	2.30	0.6	2.70	0.450	2.222	0.435	-0.347	0.362
5	2.00	0.8	3.00	0.375	2.667	0.500	-0.426	0.301
5	1.80	1.0	3.20	0.320	3.125	0.556	-0.495	0.255
5	1.70	1.2	3.30	0.275	3.636	0.588	-0.561	0.230
5	1.67	1.4	3.33	0.237	4.219	0.599	-0.625	0.223

Langmuir equation is given as

$$q_e = \frac{abC_e}{(1+bC_e)}$$

In the linearized form.it can be given as

$$\frac{1}{q_e} = \frac{1}{ab}.(\frac{1}{C_e}) + \frac{1}{a}$$

Where, q_e is the amount of solute adsorbed per unit weight of material, a is the maximum adsorption capacity, b is the Langmuir constant, and Ceis the equilibrium solute concentration.

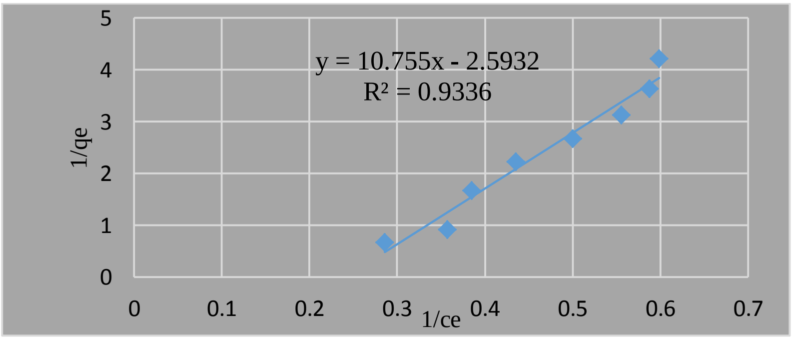

Figure 6. Plot of Langmuir isotherm for adsorption of fluoride using bagasse powder

Figure 6 shows the plot of Langmuir isotherm of fluoride sorption using bagasse powder. The value of slope (1/ab) and intercept (1/a) is found from the graph. From the values of slope and intercept, the value of maximum adsorption capacity (a) is found to be 0.3856 and Langmuir constant (b) is found to be 0.3585.The value of Correlation coefficient is found to be 0.9336 showing that Langmuir isotherm shows a good fit to the adsorption mechanism of fluoride using the bagasse powder.

5.2Freundlich Isotherm

Freundlich adsorption isotherm is the isotherm which studies the adsorption of solutes from the liquid onto a solid adsorbent. The major assumptions of the Freundlich isotherm theory is that it suggests that multiple sites are involved having different adsorption energies Freundlich isotherm equation is given by

$$q_e = K_f Ce^{1/n}$$

The logarithmic form of the equation becomes

$$\textbf{Log } q_e = \frac{1}{n}\textbf{Log } C_e + \textbf{Log } K_f$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g),Ce is the equilibrium solute concentration (mg/l),K_f is the measurement of the adsorption capacity (mg g-1) based on Freundlichisotherm, n is the adsorption equilibrium constant (Bart Van der Bruggen, 2017).The ability of Freundlich model to fit the experimental data was examined. Plot between Log C_e and Log q_e was drawn to generate the intercept value of K_f and the slope of n as shown in the figure below

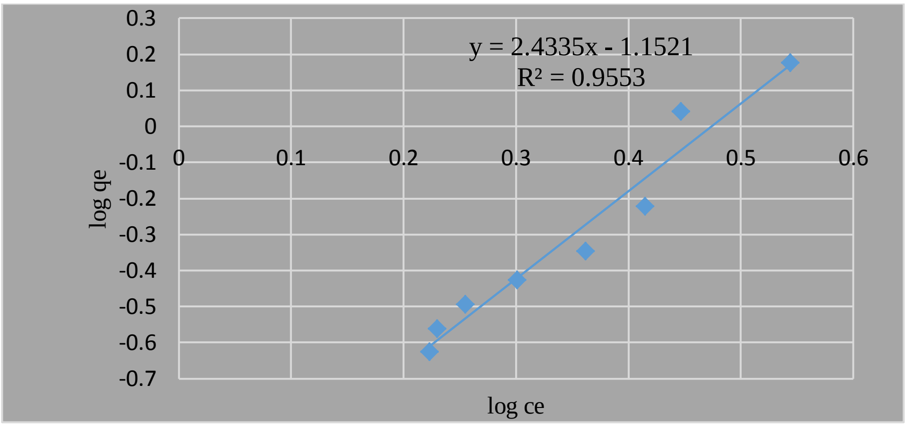

Figure 7. Plot of Freundlich isotherm for adsorption of fluoride using bagasse powder

Figure 7 shows the plot of Freundlich isotherm of fluoride sorption using bagasse. The values of slope and intercept are read from the graph. The values of $K_f$and n are calculated from the intercept and slope of the graph respectively as 0.0704 and 0.411.The correlation coefficient (R^2) is found to be 0.9553 which shows that Freundlich model of adsorption fits to the adsorption process in excellent way.

6.Adsorption Kinetics

Kinetic modelling is a very helpful study which helps in finding the sorption rates and also in determining the rate constants of the reaction occurring during the study characterizing the probable reaction mechanisms (John.F.Corbett, 1972). Theadsorption kinetics was studied using the pseudo first order and pseudo second order models. The values of the rate constants K_1 (/min) and K_2 (g/mg-min) was determined from the respective graphs of pseudo first order and pseudo second order models. For pseudo first order, graph was plotted between log (q_e-q_t) and while for pseudo second order, graph was plotted between t/q_t and t.q_e is the equilibrium concentration (mg/g), qt is the concentration of adsorbate at time t (mg/g) and t is time in minutes.

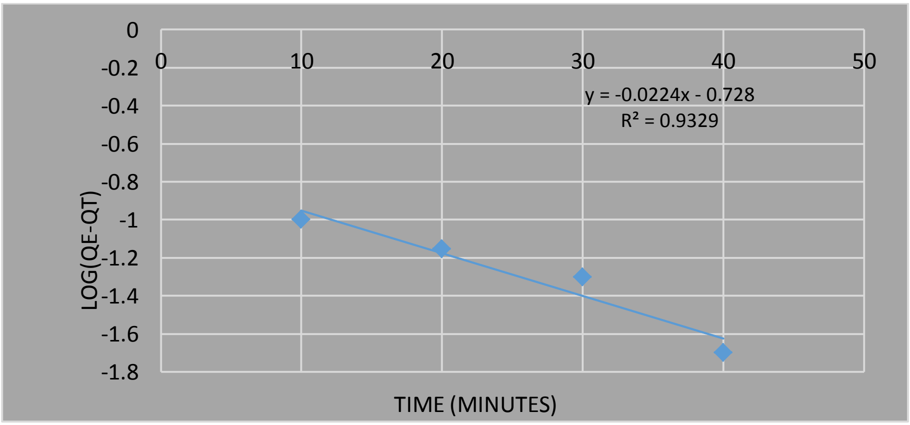

Figure 8: Pseudo first order plot of sorption kinetics for removal of fluoride byBagasse powder

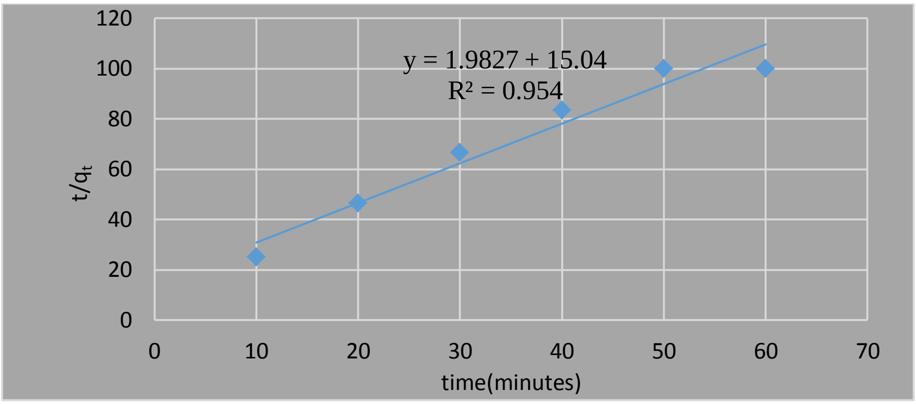

Figure 9.Pseudo second order plot of sorption kinetics for removal of fluoride by bagasse powder

The value of rate constant for Pseudo second order kinetic theory (K_2) =0.260 gm.min/mg is more than rate constant value of Pseudo first order kinetic theory (K_1) =0.0515 /min.Also, the value of Correlation coefficient (R^2) obtained for the Pseudo second order is 0.954 which is more than Correlation coefficient (R^2) obtained for the Pseudo first order which is 0.9329.Hence, it can be inferred that Pseudo second order kinetics better represents the fluoride sorption by the bagasse. The qe (exp) and the qe (calc) values from the pseudo-second-order kinetic model are very close to each other. The calculated correlation coefficient (R^2) is also closer to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetic model. Therefore, the sorption can be estimated more properly by the pseudo-second-order kinetic model as compared to the pseudo-first-order kinetic model for the fluoride removal using bagasse.

7. Conclusions

The bagasse powder is used for removing the fluoride from the groundwater by the mechanism of adsorption. Bagasse powder adsorbs fluoride ions on its surface.Based on the results on the study, it can be concluded that optimum conditions for maximum removal of fluoride from water is at adsorbent dosage of 12 g/l, optimum pH was found 7 and optimum contact time was evaluated to be 50 minutes. The adsorption mechanism followed the Freundlich isotherm model which assumes the multiple sites are involved in the adsorption and adsorption energies are different. In addition, the adsorption kinetics followed the pseudo second order model which signifies the chemisorption i.e. adsorbate is adsorbed on the adsorbent particles by the formation of hydrogen bond between them. The bagasse powder has high potential to be used as defluoridating agent as it is cheaply available and the methodology adopted is also cheap. In rural areas, bagasse dust can be efficiently employed to defluoridated water in high fluoride content areas. Also, the adsorption of fluoride using bagasse powder follows the Freundlich equation.

References

1. John F. Corbett (1972),"Pseudo first-order kinetics", Chem. Educ. 1972, 49, 10, 663.
2. WHO, 2004.
3. Fantaye Wondwossen, Anne Nordrehaug Åstrøm, Kjell Bjorvatn, Asgeir Bårdsen (2004) "The relationship between dental caries and dental fluorosis in areas with moderate- and high- fluoride drinking water in Ethiopia" , Community Dentistry and Oral Epidemiology, 32 (5), 337-344, 2004.
4. Jamodei AV, Sapkal VS, Jamode VS (2004).Defluoridation of water using inexpensive adsorbents. J Ind Inst Sci. 2004;84:163-71.
5. Naba Kr Mondal, RiaBhaumik, Arnab Banerjee, Jayanta Kr Datta, TanmoyBaur (2011), "A comparative study on the batch performance of fluoride adsorption by activated silica gel and activated rice husk ash", International Journal of Environmental Sciences, Volume 2, No 3.
6. N. Gandhi, D. Sirisha, K.B. Chandra Shekar and SmitaAsthana (2012), "Removal of Fluoride From Water And Waste Water By Using Low Cost Adsorbents", International Journal of ChemTech Research Vol.4, No.4, pp 1646- 1653.

7. R. Bhaumik, N. K. Mondal, B. Das ,P. Roy, K. C. Pal, C. Das, A. Banerjee, and J. Datta (2012), "Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies", E-Journal of Chemistry, volume 9(issue3), pg1457-1480.
8. Madhumita Bhaumik, Hyoung J. Choi, Mathapelo Pearl Seopela, Arjun Maity (2014), "Highly Effective Removal of Toxic Cr(VI) from Wastewater Using Sulfuric Acid-Modified Avocado Seed, Industrial & Engineering Chemistry Research 53(3):1214–1224, 2014.
9. Suman Mann, Dr Anubha Mandal (2014), "Removal of Fluoride from Drinking Water Using Sawdust", Int. Journal of Engineering Research and Applications, ISSN : 2248-9622, Vol. 4, Issue 7(Version 2), July 2014, pp.116-123.
10. S.S Waghmare and T.Arfin, (2015), Fluoride removal from water by calcium materials- a state of the art review, International journal of Innovative Research in Science, Engineering and Technology, 4(9), pp.8090-8012.
11. SutapaChakrabart, H.P.Sarma (2016),Defluoridation of contaminated drinking water using Neem charcoal adsorbent kinetics and equilibrium studies, International journal of chem tech Research Coden (USA) vol.4, N0.2 pp 511-516, ISSN : 0974-4290.
12. PS Ghosal, AK Gupta (2017),"Determination of thermodynamic parameters from Langmuir isotherm constant-revisited", Journal of Molecular Liquids 225, 137-146, 2017.
13. Xin Li, Yuxin Liu, Jing Wang, Jorge Gascon, Jiansheng Li and Bart Van der Bruggen (2017)," Metal–organic frameworks based membranes for liquid separation", Chem. Soc. Rev., 2017,46, 7124-7144.

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