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Research Paper

Bio-inspired adsorption of fluoride by rice husk activated carbon @ Al composite from aqueous solutions: Application in groundwater samples

Mallikarjuna Ruchir Grandhi[1] and Vaddi Dhilleswararao[2]*
[1](*Studying in year-12, Jumeriah College, 19th St-Al Safa 1-Dubai, United Arab Emirates)*
[2](*Department of Chemistry, G M R Institute of Technology, Rajam-532127, Srikakulam District, Andhra Pradesh, India)*
Corresponding Author: Vaddi Dhilleswararao

Abstract: *Contaminated groundwater influences the health of human beings directly or indirectly because of the presence of different chemical components in the water. The main important considerable constituent in water is fluoride. Fluoride has both valuable and perilous effect for human wellbeing. Hence, there is a necessity for fruitful fluoride removal from water. In this work, the Rice husk activated carbon @ Al composite material is used as a bio-adsorbent for fluoride removal. Rice husk is a bio-waste; choosing rice husk is a good choice because of the more availability, economic feasibility, less biodegradation, the existence of surface groups as well as no discharge of soluble pollutants into the water. On batch mode studies, the percentage removal of fluoride depends on the variation of some parameters for example pH, bio-adsorbent dosage, and contact period and fluoride concentration. 89% of fluoride adsorption occurs under optimum conditions. The possible mechanism might be a strong columbic interaction among Al^{3+} and F^- as well as fluoride exchange with the surface hydroxyl groups of rice husk activated carbon @Al composite. The application of the bio-adsorbent is to successfully reduce the fluoride content in groundwater samples to below the desirable limits according to WHO and BIS. The desorption studies demonstrated that sodium hydroxide is a regenerating agent and adsorbent is reused for several adsorption-desorption cycles. Hence, the prepared bio-adsorbent in this work is confirmed to be one of the alternative materials as it is economically doable and readily executed in water treatment technology.*

Keywords*: Rice husk, activated carbon, Bio-adsorbent, fluoride adsorption*

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I. INTRODUCTION

The earth is renowned as a "Water planet" since about 74% of the earth surface is covered by frozen water. Water is the principal constituent of all living beings. It is usually available from two important resources such as surface and underground. About, 97.2% is salty water, and only 2.8% is fresh water on the earth [1]. The world's freshwater is about 0.08% and is exploited by human deeds owing to the exponential demand for industrialization, sanitation, and agriculture. The rest of the availability of pure water is considered a national strength and it is the most pivotal component of all the living beings on the earth. Fresh water is the prime need for human beings, and it is considered as an essential factor that is directly or indirectly connected with social and economic development. Hence, a flawless and trustworthy supply of water is essential to ensure a high quality of life and a strong economy.

Groundwater is generally said to be a secure resource of safe potable water, and is one of the main resources of drinking water and also used for domestic, irrigation and industrial purposes in many regions of the world [2], but the groundwater is mainly considered to be prone to physicochemical pollution caused by lack of compact adjacent drainage system, seepage from discharge bearing water body and contaminated by industrial waste discharge, applied fertilizers in cultivation, etc. The quality of water is influenced by a wide scope of natural as well as anthropogenic impacts that alter the concentration of chemical constituents in the groundwater.

Out of the different pollutants in water, one of the significant pollutants is fluoride. Fluoride is usually obtained in the groundwater due to the dissolution of fluoride-containing granite rocks, shale etc. Fluoride in potable water is both a valuable and perilous contribution to human wellbeing. Fluoride in groundwater generally has low concentrations and helps to avoid tooth rot in children [3]. According to WHO-2017[4] and BIS-2012[5], the allowable limit of F^- in the potable water should be <1.5ppm and <1.0ppm respectively. Epidemiological examinations in the first half of the twentieth century demonstrated that normally occurring F^- in water could be useful and detrimental to dental health. Fluoride is an essential nutrient for humankind at low levels. Long-term utilization of 1.5–2.0 mg l^{-1} of F^- water may prompt mottling in patients with long-standing renal disease or polydipsia, mottling of teeth and dental fluorosis etc.

Fluorosis is a basic universal health problem in 24 nations [6]. Among them, China and India [7] are the worst affected. In India, around 20 million residents were truly affected by fluorosis. Endemic fluorosis is common in a few states in India such as Haryana, Karnataka, Punjab, Gujarat, Bihar, Maharashtra, Uttar Pradesh, Telangana Tamil Nadu and Andhra Pradesh [8]. In Andhra Pradesh, 11 districts out of 13 districts have suffered due to excess fluoride [9]. Excess fluoride content was also noticed in groundwater's of some of the villages in eight mandals(G. Sigadam, Rajam, Ponduru, Tekkali, Nandigam Laveru, meliaputti, santhabommali and Ranastalam) of Srikakulam district[10] in Andhra Pradesh and are not an exemption to this menace and mainly depends on fluoride-containing water.

Due to these destructive impacts on people, required precautionary measures should be taken to keep away from the utilization of excess fluoride. In this way, there is a necessity for fruitful fluoride removal developments that can be essentially applied to throughout the planet [11]. Different methods have been represented for the fluoride removal in contaminated water and the techniques like electro-dialysis, precipitation, reverse osmosis, electro de-fluoridation, membrane, filtration and ion exchange methods etc.[12,13,14] are used. These methods (shown in Table-1) have some drawbacks like the quantity of sludge disposal is extremely high, separation for high concentrated solutions is tricky, operation costs are very high.

Table-1: The advantages and drawbacks of some water treatment techniques

Removal Method	Advantages	Drawbacks
Chemical Precipitation: It involves the adding of suitable chemicals to accomplish the precipitation of required target ions	Low-cost, easy to operate and most of the metal ions can be removed.	The quantity of sludge disposal is extremely high, separation for high concentrated solutions is tricky
Chemical Coagulation: It involves the adding of positively charged coagulants to destabilize the negatively charged surface of the solid entities.	Cheap and settle of sludge and dewatering	development of large-sized particles
Ultra Filtration: It is a membrane filtration where concentration or pressure gradients are utilized to separate through a semi-permeable membrane	Utilization of chemicals is less, waste production is reduced.	Flow rates are very low, initial and operational costs are significantly high.
Electro-dialysis: It is the separation of heavy metal ions by the cation as well as anion-selective membranes across the pathway of an electric current	Equipment occupies less space, High efficiency for the removal of ions and the process is easy.	Operation costs are very high; Membranes are blocked by the metal hydroxides formation.
Ion- Exchange: It is a procedure in which solid surface containing ions on the surface are exchanged with the ions in the solution by electrostatic forces.	Metal recuperation is effective.	Economically high cost, Sensitive to particular ions.
Reverse Osmosis: It is a semi-permeable membrane process which is pressure-driven to retain the high concentration on one side and allows the solvent molecules to low concentration to purify the wastewaters, contaminated waters etc.	An efficient removal method where pure effluent is attained	High cost, the membrane should be changed for a particular period. Membrane scales up at elevated pressures are necessary, high sensitivity to total suspended solids and organic matters.
Adsorption: This process involves the surface accumulation of solute particles in a solid-liquid interface.	Relatively simple, flexible, comfortable design, ease of operation and cost-effectiveness. No formation of secondary effluent and sludge generation and also has an advantage to other methods to remove the constituents even in dilute solutions. An opportunity of recovering the required components. Activated carbons prepared from waste materials, they are of economically low cost.	Adsorbent acting as a key function in the performance of the adsorption of required ion from the solution.

Hence, adsorption method is currently perceived as a powerful and economical technique for the expulsion of fluoride from waters. Adsorbent, for example, activated carbon is a splendid adsorbent with better chemical properties, high porous nature, large surface area, more active sites for adsorption. Commercially accessible activated carbons are extremely expensive, therefore; activated carbon prepared with economically low-cost materials could radically reduce the cost of an adsorption process, which is an option for the fluoride removal from waters. In general, the adsorption mechanisms are associated with surface complexation, chemisorptions, diffusion through micropores, electrostatic interactions and ion exchange.

Materials locally available from industrial wastes and agricultural wastes such as Mangifera Indica seed shell[15], Activated Carbon prepared by the barks of Ficus Racemosa[16], Activated carbon of bael (Aegle marmelos) shell[17], wheat straw and eupatorium adenophorum, Prosopis Juliflora bark, rice straw, African biomass residues, sugarcane baggage and sawdust etc. have been utilized to prepare activated carbons as an adsorbent to evaluate their suitability in the field of fluoride removal. The operational costs of adsorption are principally constrained by the expense of the adsorbent, and hence there is a developing enthusiasm for looking for alternative materials in activated carbon preparation.

To increase adsorption effectiveness, the modification of existing carbon-based adsorbents with proper chemicals has been researched with prominent results proposing that the alteration of activated carbon material can remove fluoride successfully [18, 19]. Fluoride has a great affinity towards metal ions, for example, Al^{3+}, La^{3+} and Fe^{3+}[20]. Hence, activated carbon blended with metal exhibits significant potential for fluoride removal from waters.

However, a close examination of the literature discloses that most of the available materials have some disadvantageous for example, more expensive, low efficiency, difficult to make, low efficiency and formation of hazardous products etc. According to the seriousness of the problem and lack of a suitable economical process for the fluoride removal, Preparation of low-cost adsorbent using rice husk as a bio-antecedent is taken up since the economic viability is a requirement for the decontamination of water in rural areas. The rice husk is widely available in the rice mills as biowaste. Choosing rice husk is a good choice because of the less biodegradation, existence of surface groups as well as no discharge of soluble pollutants into the water. In addition, using low-cost aluminium metal ion as an active binding site for fluoride interaction might enhance the adsorption effectiveness towards fluoride ion.

This project is intended to examine the efficiency of rice husk activated carbon @ Al metal composite material as a bio-adsorbent for fluoride removal from aqueous solutions. The basic parameters considered are varying pH, adsorbent dosage, time of contact period and varying fluoride ion initial concentration. Bio-inspired adsorption of fluoride in groundwater samples also examine.

II. MATERIALS AND METHODS

2.1) Preparation of Rice husk activated carbon @ Aluminium composite material as an adsorbent

Rice husk is collected from the local region from the rice mill, and it is air-dried under sunlight for around five days. The dried rice husk is ground into a uniform powder and is mixed with conc.H_2SO_4 in a weight ratio of 1:1.8(rice husk powder: H_2SO_4)[21] followed by heating in a furnace(muffle furnace) at 300°C for two hours to obtain an activated carbon material. The activated carbon material is washed with double distilled water several times until free from acidic molecules and it is dried at 110 °C in an oven. To the dried activated carbon material, aluminium metal powder is blended in the weight ratio 10:1(activated carbon: Al powder) in a flask followed by the addition of concentrated hydrochloric acid drop by drop with constant stirring until the aluminium metal powder is thoroughly mixed with rice husk activated carbon to form a precipitate. The obtained precipitate is washed with double distilled water several times until free from acid. The ensuing material (rice husk activated carbon @ Al composite) is dried and ground into a particle size of <75 μm using mesh and is stored in a desiccator for further use.

2.2) Chemicals and instruments required

Analytical reagent (AR) grade aluminium powder is used for metal embedded in the activated carbon material. TISAB (total ionic strength buffer) solution, Sodium fluoride salt is taken for the preparation of the stock fluoride solution. Ion analyser with fluoride electrode (Cyber Scan 2100, Eutech) is used for fluoride determination; pH meter (model 335, Systronics) is utilized to measure the solution pH. 0.1M NaOH and 0.1M HCl solution are utilized to adjust the pH of the solution.

2.3) Determination of Fluoride by Ion-selective electrode method

a) Preparation of Standard Stock fluoride (1000ppm) solution:

0.5526 g of sodium fluoride salt is taken in a 250ml volumetric flask and is dissolved with double de-ionized water and again makeup with de-ionized water up to the mark of the flask.

The concentration of fluoride (ppm) is calculated by the expression

$$\text{Conc. of fluoride (ppm)} = \frac{\text{weight of NaF substance}}{\text{Volume of the solution}} \text{X} \frac{\text{atomic weight of fluoride}}{\text{molecular weight of NaF}} X1000000$$

b) Preparation of intermediate Fluoride (100ppm) solution:
The intermediate fluoride solution (100ppm) is prepared from the stock solution by proper dilutions with double distilled water using the following equation-1.

$$C_1V_1 = C_2V_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where 'C_1' is the stock fluoride solution (1000ppm), 'C_2' is the required concentration (100ppm), 'V1 (ml)' is the volume of the stock solution taken, and 'V_2 (ml)' is the required volume of the solution.
Here, 10ml of 1000 ppm of fluoride solution is taken into a 100ml volumetric flask and add distilled water with constant shaking up to the mark to get 100ppm of fluoride solution in 100ml.
c) Preparation of working standard Fluoride (10ppm) solution
The standard working fluoride solution 10ppm is prepared from the intermediate fluoride solution (100ppm) by proper dilution with double distilled water. In this case, 10ml of 100 ppm of fluoride solution is taken into 100ml volumetric flask and add distilled water with constant shaking up to the mark to get 10ppm of fluoride solution in 100ml.

Procedure: The known concentrations of 1.0 ppm, 2.0 ppm, 3.0 ppm, 4.0 ppm and 5.0 ppm of fluoride solutions are prepared in 50ml volumetric flasks from working fluoride (10ppm) solution using the expression in equation-1. Also, unknown concentrated fluoride samples taken into a 50ml volumetric flask. These are transferred into polyethylene containers and added with 5ml of TISAB solution (adding an appropriate TISAB gives a uniform ionic strength background, breaks up fluoride complexes and adjusts pH). The fluoride ion-selective electrode is immersed in each solution, and the potential of the cell (E_{cell}) is measured as per the manual of the fluoride electrode. A graph is drawn between Log C (x-axis) and E_{cell} (y-axis). The E_{cell} values of unknown samples on the same plot are located and the corresponding Log C values are obtained. By taking antilog values of them, the concentrations of unknown F^- ion in samples are obtained.

2.4) Batch adsorption studies

In Batch mode adsorption experiments, known volume of fluoride solution (50 ml) of known concentration (10ppm) is taken into a plastic flask with a preset amount of bio-adsorbent, solution pH and time period. The solution is uniformly shaken in an orbital shaker at 150 rpm until preset time period. Then, the fluoride solution containing adsorbent is filtered, and the leftover fluoride ions in the filtrate solution is measured by the fluoride-Ion selective electrode method. The influencing parameters, for example, pH (4.0 - 9.0), bio-adsorbent dosages (5- 30 g/L of fluoride solution), time of contact (10-70 minutes), initial fluoride concentration (6-16 ppm) are varied to get optimum adsorption conditions for the optimum fluoride removal. For every experiment, one of the above said parameters is varied and other parameters are pre-set to a particular value.
The percentage removal of fluoride is measured by the following expression (1)

$$\% R = [\frac{C_i - C_e}{C_o})] \times 100 \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1)}$$

Here, 'C_i' and 'C_e' are concentrations of initial and equilibrium concentration of fluoride in ppm.

III. RESULTS AND DISCUSSION

3.1) Adsorption studies

i) *Percentage removal of Fluoride at different pH of the solution*

The solution pH is a significant factor in the adsorption of fluoride because it decides the charge of the adsorbent surface. To establish the effect pH of the solutions on the percentage fluoride removal, the batch studies at various pH levels of the solutions are carried out in the range of pH 3.00 to 9.00 by predetermined bio-adsorbent dosage (20 g/L of the 10ppm fluoride solution) and 60 minutes of time of the contact between adsorbent with the fluoride solution. The percentage removal of fluoride at different pH of the solutions is shown in Figure-1.

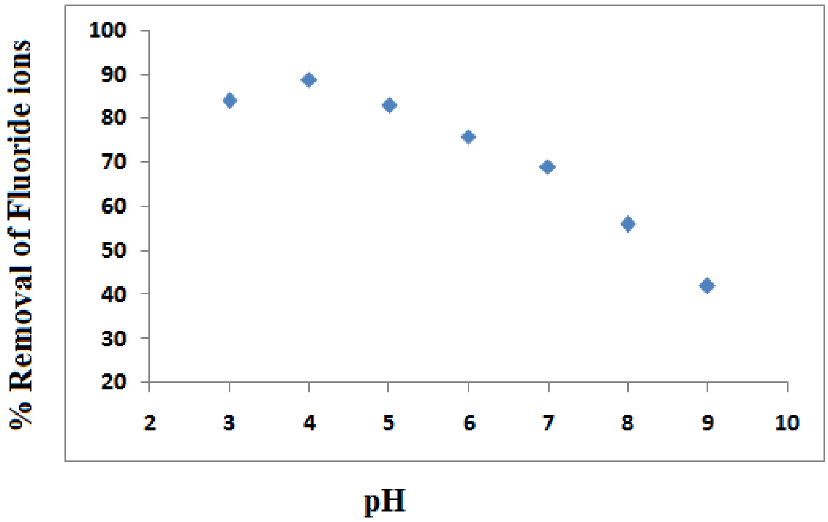

Figure-1: Variation of pH on % removal of fluoride ions

It is seen that the fluoride adsorption is maximum (89%) at the pH of 4.0. At this pH, the surface of the prepared adsorbent is positively charged thus, there is a higher scope of columbic interaction between the activated carbon @Al adsorbent with fluoride ion [20]. As the pH of the solution increases from 4.00 to 9.00, the percentage removal of fluoride decreases from 89% to 42% since the number of surface active sites is negatively charged and consequently, more electrostatic repulsions emerge. The possible fluoride removal mechanism can be a strong columbic interaction among Al^{3+} and F^- as well as fluoride exchange with the surface hydroxyl groups of rice husk activated carbon @Al composite. The possible mechanism of fluoride adsorption is shown in Figure-2.

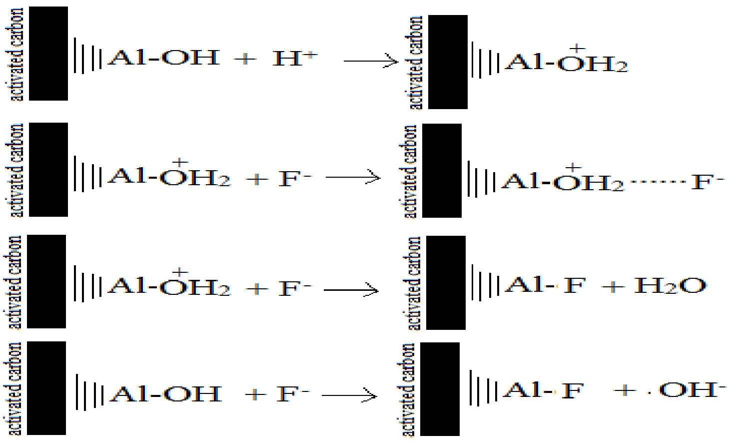

Figure-2: possible mechanism of fluoride adsorption by rice husk activated carbon@Al composite

ii) Percentage removal of Fluoride at different Bio-adsorbent dosages

The adsorption studies are performed with different adsorbent dosages (5g/L to 25 g/L of 10 ppm fluoride solution) by predetermined pH (4.00) and 60 minutes time of contact between adsorbent with fluoride solution. When there is an enhancement in the bio-adsorbent dosage from 5 to 20 g/L of 10 ppm fluoride, the fluoride adsorption on the adsorbent surface also increases, as shown in Figure-3 because there is an increment in the number of active binding sites by an increase in the adsorbent dosage. Though, further addition in the adsorbent[22] doesn't have a significant increment in the fluoride adsorption owing to the number of fluoride ions is fixed to adsorb on the surface of the adsorbent after attaining equilibrium.

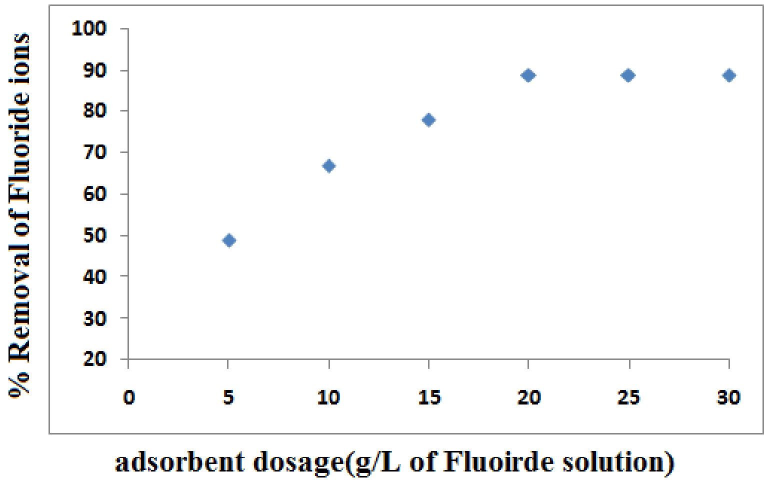

Figure-3: Variation of adsorbent dosage on % removal of fluoride ions

iii) ***Percentage removal of Fluoride at different time intervals***

The contact time between the adsorbent with fluoride solution is another important factor in adsorption examinations. The adsorption studies are performed with different time of contact from 10 minutes to 70 minutes by predetermined pH (4.00), fluoride concentration (10ppm) and adsorbent dosage (20 g/L of a fluoride solution). The results (Figure-4) reveal that the adsorption of fluoride increases by increasing contact time from 10 minutes to 60 minutes and after reaching equilibrium there is no further increment of fluoride adsorption. Since initially the number of active sites is more in the bio-adsorbent surface. The removal rate of fluoride is almost insignificant after equilibrium and might be due to the fast exhaustion of the reactive sites [23].

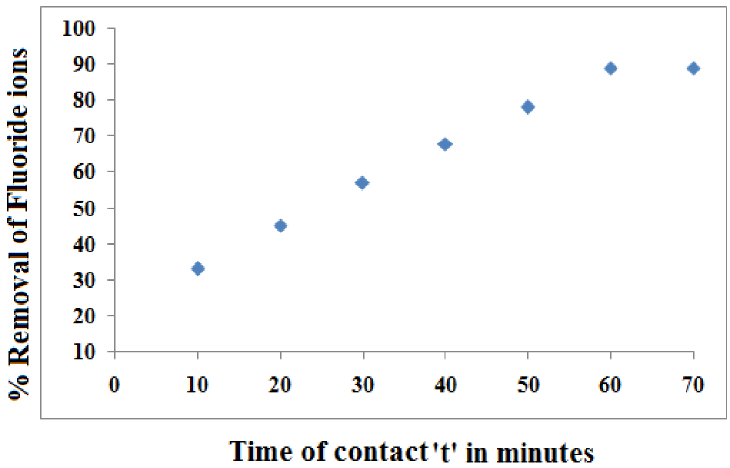

Figure-4: Variation of time of contact on % removal of fluoride ions

iv) ***Percentage removal of Fluoride at different concentrations of fluoride solutions***

The adsorption rate of fluoride is mostly dependent on the initial concentration of fluoride. The adsorption studies are performed with different concentrations of fluoride solutions from 6.0 ppm to 16.0 ppm by predetermined adsorbent dosage 20 g/L of fluoride solution and 60 minutes of the time of contact. The % removal of fluoride with different concentrations of fluoride is present in Figure-5. The experimental results reveal that 96% of fluoride removal takes place for 6ppm fluoride solution and the concentration of fluoride solution increases from 6.0 to 16.0ppm, the percentage removal decreases from 96% to 66%. Since in low concentration, the number of fluoride ions is less and these ions immediately interact with active sites present in the adsorbent and hence more adsorption takes place. As the concentration increases (fluoride ions increases), the specific active binding sites in the adsorbent are saturated and hence no further active sites are available to adsorb.

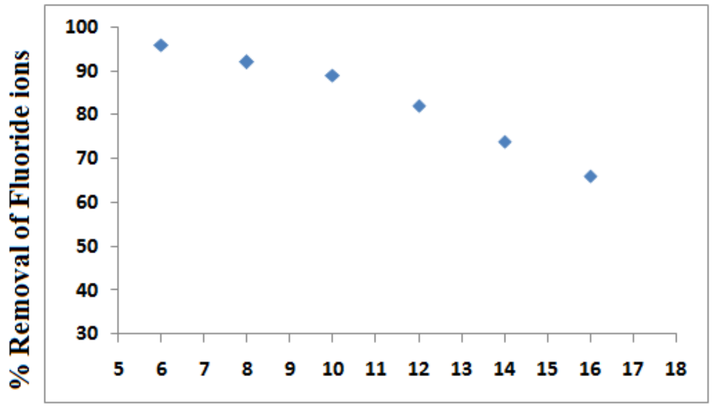

Figure-5: Variation of initial concentration of fluoride on % removal of fluoride ions

3.2) Regeneration studies

The adsorption process using an adsorbent is economical if it is regenerated and reused for several adsorptions and desorption cycles [24]. The desorption of fluoride from the adsorbent is performed utilizing 0.5M NaOH under uniform stirring for 12 hours and 96% of desorption of fluoride is obtained. The regenerated material is re-used for the adsorption of fluoride with 10ppm of fluoride solution under the same conditions. The replacement of F^- ions by $-OH^-$ ions in the adsorbent surface using sodium hydroxide is accountable to the desorption procedure. The % removal of fluoride from the regenerated adsorbent for the three successive cycles is shown in Figure-6. It is obvious that the percentage removal of fluoride is still around 80% at the third cycle, which represents that the prepared adsorbent is effectively working after regeneration. The exhausted adsorbents are used for the making of fuel briquettes which are utilized in boilers and furnaces. The formed ash might be utilized for the partial replacement of different construction supplies such as fire bricks, cement and building blocks.

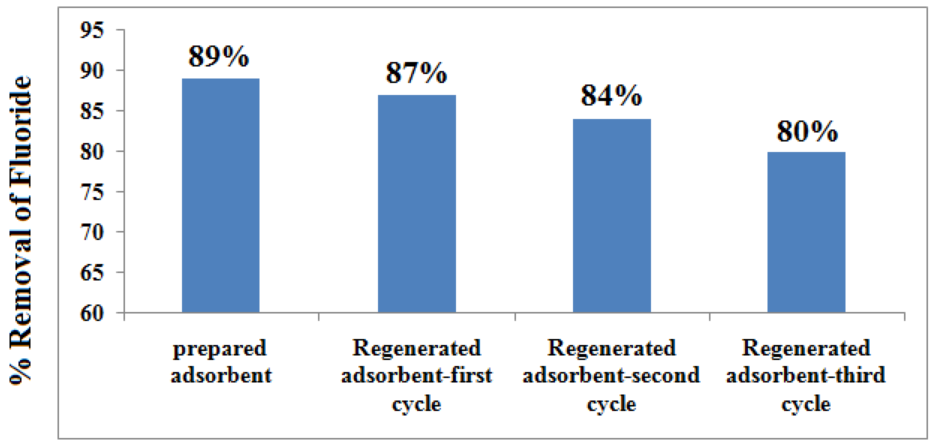

Figure-6: % Removal of fluoride with regenerated adsorbent for three successive cycles.

3.3) Application:

Removal of fluoride from groundwater samples utilizing Rice husk activated carbon@ Al composite adsorbent

The desirable limit of fluoride in potable water according to the WHO (World Health Organization) and BIS (Bureau of Indian standards) are less than 1.5ppm and 1.0ppm, respectively. The adaptability of the method developed with the prepared bio-adsorbent in this work for fluoride removal has been attempted with groundwater samples (Hand pump) collected from different locations in rural areas of Srikakulam District of Andhra Pradesh. In this work, 1gm of bio-adsorbent is directly taken into 50 ml of groundwater samples (20 g of adsorbent per liter of groundwater) and uniformly stirring the samples at 150rpm for 60 minutes under room temperatures. Then the water samples are filtered with whatmann filter papers and tested the fluoride content in the filtrate. The F^- concentration in the groundwater samples, before and after treatment with a bio-adsorbent is presented in Table 2. It is demonstrated that the adsorbent adequately decreases the fluoride in groundwater samples below the desirable limit of WHO and BIS standards. It is perceived that the procedure developed utilizing novel bio-adsorbent for fluoride adsorption in this examination is amazingly fruitful and is suitable for fluoride-rich waters in any locations.

Table-2: The concentration of fluoride in groundwater samples before and after treatment with bio-adsorbent

S.No	Groundwater collected (through Hand pump) in the villages	Before adsorption-Fluoride concentration(ppm)	After adsorption-Fluoride concentration(ppm)	% removal of Fluoride
1	Velagada Village (G.Sigadam Mandal)	2.42	0.46	80.9
2	Chadrayyapeta village (G.Sigadam Mandal)	3.13	0.72	76.9
3	Ponugutivalasa Village (Santhakavati Mandal)	1.62	0.30	81.4
4	Guravam village (Rajam Mandal)	1.63	0.32	80.3
5	Penubarthi Village (Ponduru Mandal)	1.84	0.36	80.4

IV. CONCLUSION

Rice husk activated carbon @ Al composite material proved to be a remarkably more capable and useful adsorbent for fluoride removal. The percentage removal of fluoride depends on the variation of some parameters for example pH, bio-adsorbent dosage, contact period and fluoride concentration. Maximum adsorption (89%) of fluoride occurs under optimum conditions. The possible fluoride removal mechanism can be a strong columbic interaction among Al^{3+} and F^- as well as fluoride exchange with the surface hydroxyl groups of rice husk activated carbon @Al composite. Regeneration studies reveal that the adsorbent is reusable with sodium hydroxide as a regenerating agent. The application of the prepared adsorbent is to successfully reduce the fluoride content in groundwater samples to below the desirable limits according to WHO and BIS. The overall results indicate that the prepared bio-adsorbent is one of the best materials as it is economically doable and readily executed in water treatment technology, as it doesn't need costly pre-treatment.

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