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Research article

Comparison the Efficiency of Bagas, Modified Bagas and Chitosan for Fluoride Removal from Water by Adsorption

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Abstract

Fluoride is used widely in industries such as manufacture of semi-conductors, power plants, glass production and etc and released to the environment via their effluents. The purpose of this sturdy was to compare the efficiency of low price adsorbents in fluoride removal from water. The optimum values of pH, contact time and adsorbent dosage were determined and different concentrations of fluoride were experimented in lab scale conditions for bagas, modified bagas and chitosan. Then Langmuir and Freundlich contacts were also determined based on optimum conditions. The pH value of 7, contact time of 60 min and adsorbent dose of 2 g/L were determined as optimum conditions for all three adsorbents. The most fluoride removal efficiency of 91% was obtained for modified bagas in optimum conditions. Based on data obtained in this study, it can be concluded that adsorption by modified bagas is an efficient and reliable method for fluoride removal from liquid solutions.

Keywords: Fluoride, Flourosis, Adsorption, Chitosan, Modified bagas.

1 Introduction

Fluoride is a natural element among mineral materials, geological sediments and natural water systems which enters food chain via potable water or feeding vegetations [1]. Fluoride and its compounds are easily available and are widely used in industries such as manufacture of semi-conductors, power plants, glass and ceramic production, uranium purification, electrochemical industries, production of high purity graphite, manufacture of rubber, production fertilizers, metal finishing, alumina electrolysis and etc and released to the environment via their effluents. Discharge of these effluents to the surface waters can lead to the contamination of underground waters. Therefore, concentrations of fluoride ions in underground waters are more than acceptable limits in many areas in the world [2-3].

Fluoride content of water, based on its concentration and total amount of uptake can be beneficial or harmful. Fluoride in the concentration range of 1-1.5 mg/L is especially beneficial for children under 8 years, because prevents dental decay. Physiological effects of excess fluoride uptake on human body are widely studied. Generally, fluoride in the acceptable concentration is necessary for prevention of dental decay and health of bones in body [4]. Fluoride concentrations of more than 1-1.5 mg/L affect the metabolism of elements such as calcium and potassium in body. Adverse health effects of exposure to excess fluoride are proven. These effects are more serious in hot weather areas, where people consume more water, and also the concentration of fluoride increases because of evaporation [4-5]. Problems of fluoride contamination in water is more serious in rural areas and towns, especially in developing countries. According to WHO guidelines, acceptable fluoride concentration in water is 1.5 mg/L. [6]

Different treatment methods such as chemical precipitation by Ca and Al salts, adsorption by activated alumina, alum, charcoal, ash, use of 3-calcium phosphate granolas, ionic exchange resins, membrane processes such as nanofiltration, reverse osmosis and electrodialysis are experimented for fluoride removal. By the way, the most common method has been used for fluoride removal is adsorption by different adsorbent such as activated carbon, activated alumina and chitosan. Adsorption has been considered as an economic and common method in developing countries for defluoridation of water. The successfully of adsorption is dependent to application of efficient, economic, viable and reliable adsorbents and public acceptance. The criteria for selection of an adsorbent are adsorption capacity and economical aspects [15]. Different adsorbents like activated bockside [15], activated alumina [8], brick powder [9], enriched titanium bockcite [10], ferric oxide [15], and enriched zeolite by aluminum [21] are studied in different researches for defluoridation of water, which has shown variable removal efficiencies in the range 50 -90% for raw water fluoride concentrations of 5-25 mg/L. Tung et al (2009) studied the performance of activated alumina for defluoridation of water by adsorption [11]. Sairam et al (2009) studied defluori dation of water using magnesia/chitosan composite. The equilibrium data were fitted with isotherm and kinetic models [12]. Jagtab et al (2009) studied the efficiency of chitosan for removal of fluoride from drinking water. The maximum removal efficiency was obtained in pH of 6.7 and contact time of 20 min. They concluded that the presence of chloride, sulfate, carbonate and bicarbonate ions in drinking water greatly affect the uptake of fluoride, indicating that these anions compete with sorption of fluoride [13]. In another study, worku et al (2007) used residuals of alum production for defluoridation. The maximum removal efficiency of 85% was obtained at adsorbent dose of 16 g/L, initial fluoride concentration of 10 mg/L and pH range of 3-8 [14]. Considering the other researches, the efficiency of three adsorbents include modified bagas, bagas and chitosan were experimented in this study because of low cost and ease of access. The main purpose of this study was to determine the efficiency of fluoride removal with adsorption process by modified bagas, bagas and chitosan as adsorbent, and also the determination the optimum conditions of factors affecting the operation such as pH, contact time and adsorbent dose and comparison of results.

2 Materials and Methods

2.1 Chemicals

The chitozan was purchased from Sigma. The bagas was also purchased from Karun Corporation, Iran. Bagas was first milled and then passed through a 2 mm screen. In order to modify the bagas, 50 g bagas was mixed with a 0/1 M $NaHCO_3$ solution for 120 min. Then the mixture was filtered to recover the bagas and scoured for several times with deionized water and dried in 90 ^oC for 180 min [16].

2.2 Experimental procedure

First, the optimum pH value was determined. A solution containing 5 mg/L fluoride and 2 g/L adsorbent (bagas, modified bagas and chitozan) was used in contact time of 120 min. Before adding the adsorbent, the pH value of solution was adjusted to 3, 5, 7, 9 and 11 with H_2SO_4 or NaOH. The mixtures were placed on a stirrer with 200 rpm for 120 min. After this time, the samples were passed through a Wattman filter of 0/45 µm and the fluoride adsorption was determined by spectrophotometer. Once the pH value was optimized, the optimum contact time was determined in constant conditions of 5 mg/L fluoride and 2 g/L adsorbent dosage and the reaction times of 0, 15, 30, 45, 60, 90, 120 and 240 min. At certain intervals, the samples were passed through a Wattman filter of 0/45 µm and the fluoride adsorption was determined by spectrophotometer. Once the optimum pH and contact time were determined, the optimum adsorbent dosage was examined in present of constant fluoride concentration of 5 mg/L. Five concentrations of adsorbents (bagas, modified bagas and chitozan) including 1, 2, 3, 4 and 5 g/L were experimented. Then the fluoride concentrations were determined with spectrophotometer. Finally, at the optimum conditions, various fluoride concentrations 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 mg/L were investigated.

2.3 Isotherm studies

The equilibrium between adsorbed fluoride ions and free fluoride ions in solution can be described by adsorption isotherm models such as the Langmuir and Freundlich model.

2.3.1 Freundlich model

Equation 1 illustrates mathematical model of Freundlich isotherm [17-18]:

$$q = KC_e^{\frac{1}{n}} \tag{1}$$

Where q (mg/g) is the amount of adsorbed fluoride ions per unit weight of adsorbent and C_e (mg/L) is concentration of free fluoride ions in solution. Moreover, n and K are the Freundlich constants, and are related to the sorption intensity and sorption capacity, respectively. A straight line of q versus C_e indicates that the Freundlich isotherm model is a suitable representation of the adsorption process. The linear form of Freundlich isotherm is as below equation:

$$lnq = lnK + \frac{1}{n} C_e \tag{2}$$

2.3.2 Langmuir model

The mathematical model of Langmuir isotherm is shown by equation 3:

$$q = \frac{Bq_m C_e}{1 + BC_e} \tag{3}$$

Where q_m (mg/g) is the maximum amount of the fluoride ions per unit weight of adsorbent and B (L/mg) is related to the affinity of the binding sites. A straight line of 1/q versus $1/C_e$ indicates the suitability of Langmuir isotherm model for describing fluoride adsorption. The linear form of the Langmuir isotherm model is shown in equation 4:

$$\frac{1}{q} = \frac{1}{Bq_m} \frac{1}{C_s} + \frac{1}{q_m} \tag{4}$$

2.5 Analytical methods

The amount of adsorbed fluoride ions (in mg fluoride per unit weight of adsorbent) were calculated according to equation 5:

$$q = \frac{(C_0 - C_e)V}{M} \tag{5}$$

Where q is the amount of fluoride adsorbed onto the adsorbent (mg/g), C_0 and C_e are the initial and final concentrations of fluoride ions in solution (mg/L), respectively. In addition, V is the volume of the solution (L) and M is the weight of the adsorbent (g). The fluoride concentration was determined by spectrophotometry at 570 nm [19]. The pH and temperature were determined using a digital pH meter and thermometer respectively.

3 Results and Discussion

3.1 Determination of optimum pH

The results of determination of optimum pH of fluoride removal by adsorption process are presented in figure 1.

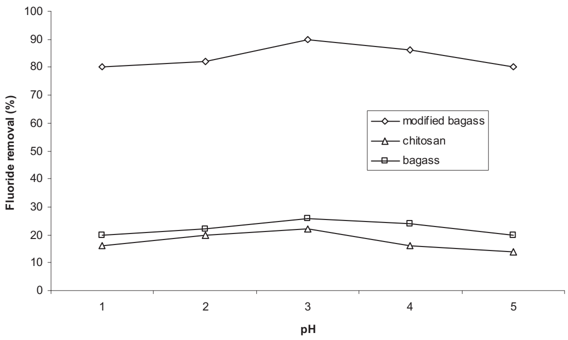

Figure 1: Fluoride removal efficiency in variable pH and constant fluoride concentration of 5 mg/L (Adsorbent dosage = 2 g/L)

The most removal efficiency of 26 % (± 0/062) for bagas at contact time of 120 min was obtained in pH value of 7. When chitozan was used as adsorbent, the most removal efficiency of fluoride in contact time of 120 min and the pH value of 7 was equal to 22% (± 0/036). In the same operational conditions, the efficiency of modified bagas was equal to 90% (± 0/13). The experiments were continued with the most efficient pH value of 7 as the optimum value.

3.2: Determination of optimum contact time

The results of contact time optimization in optimum pH value for all three adsorbents are presented in figure 2. The most removal efficiencies bagas and modified bagas in optimum pH value of 7 and contact time of 240 min, were 30 % (± 0/047) and 95 % (± 0/36), respectively. The observed removal efficiencies of fluoride at the same conditions, but contact time of 120 min for bagas and modified bagas were 28 % (± 0/093) and 94% (± 0/18) , respectively. The efficiency of chitozan for fluoride adsorption in contact times of 120 min (± 0/098) and 240 min (± 0/082) was 20%. Also the reaction time of 60 min was investigated. According to the data obtained for this time, including removal efficiencies of 91% (± 0/53), 22% (± 0/035) and 16% (± 0/067) for modified bagas, bagas and chitozan respectively, the contact time of 60 min was determined as the optimum value and the equilibrium time for final experiments, because favors the shorter time of reaction and the removal efficiency for modified bagas as an adsorbent is still more than 90%.

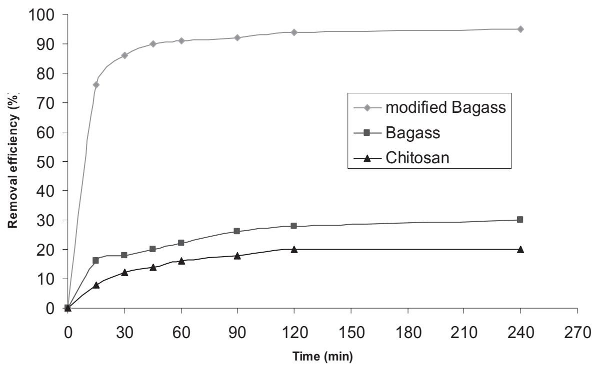

Figure 2: Fluoride removal efficiency in optimum pH, constant fluoride concentration of 5 mg/L and variable contact times (Adsorbent dasage = 2 g/L)

3.3 Determination of optimum adsorbent dosage

The results of adsorbent dosage optimization in optimum pH and contact time for fluoride concentration of 5 mg/L are presented in figure 3. It was observed that the fluoride removal increased with the increase in the dosage of the adsorbent for all three adsorbents including modified bagas, bagas and chotozan. The most fluoride removal in optimum pH and contact time for bagas, was about 44% % (± 0/03) in adsorbent dosage of 5 g/L. The efficiency of chitozan in the same conditions was 28% (± 0/073). For modified bagas, the removal efficiency in adsorbent concentrations of 2 and 5 g/L were 91 % (± 0/27) and 95% % (± 0/53), respectively. Because of the removal efficiency of more than 90% and the less adsorbent usage, the dosage of 2 g/L was determined as the optimum value.

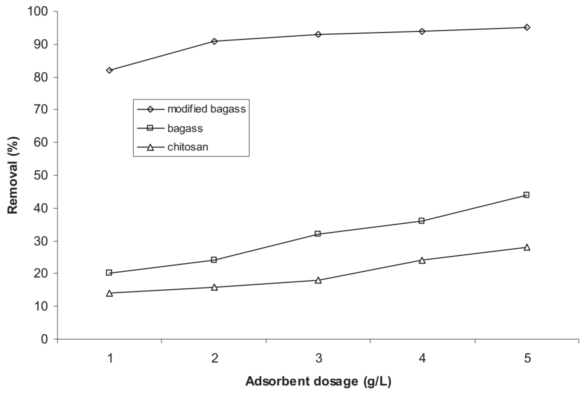

Figure 3: Fluoride removal efficiency in optimum pH and contact time, constant fluoride concentration of 5 mg/L and variable adsorbent dosages

3.4 Fluoride removal efficiency in optimum conditions

The results of fluoride removal efficiency in optimum conditions and variable fluoride concentrations are shown in figure 4. The least and the most fluoride removal efficiency for bagas were observed in feed fluoride concentration of 18 mg/L by the value of 13/3% (± 0/023) and 2 and 4 mg/L by the value of 25% (± 0/062), respectively.

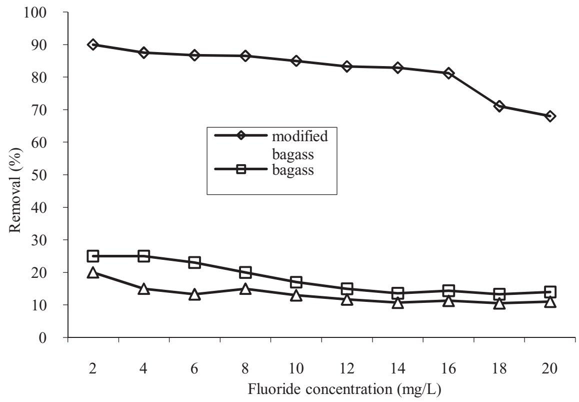

Figure 4: Fluoride removal efficiency in optimum pH, contact time and adsorbent dosage and variable fluoride concentrations

The least and the most fluoride removal efficiency for chitozan were observed in feed fluoride concentration of 18 mg/L by the value of 10/5% (± 0/052) and 2 mg/L by the value of 20% (± 0/043), respectively. The least and the most fluoride removal efficiency for modified bagas were achieved in feed fluoride concentration of 20 mg/L by the value of 68% (± 0/86) and 2 mg/L by the value of 90% (± 0/14), respectively

3.5 Adsorption isotherms

The overall trends of results indicate the decrease of fluoride removal efficiency along with influent fluoride concentration increase for all three adsorbents. The results of Langmuir and Freundlich isotherms equations and constants are presented in table 1. The Langmuir constants B and q_m were determined 0/097 L/mg and 2/034 mg/L with correlation coefficient of 0/98 for bagas and 0/095 L/mg and 1/463 mg/L with correlation coefficient of 0/97 for chitozan, respectively. Also the Langmuir constant B and q_m were determined 0/543 L/mg and 9/033 mg/L respectively, with correlation coefficient of 0/99 for modified bagas. In a study by Nigusie et al (2007), the Langmuir constants B and q_m were 0/168 L/mg and 153/8 mg/L, respectively [8].

Table 1: The Langmuir and Freundlich coefficient

Adsorbent	Langmuir			Freundlich		
	B	q_m	R^2	k	n	R^2
Modified bagas	0.543	9.033	0.99	2.812	1.699	0.93
Bagas	0.097	2.034	0.98	0.231	1.623	0.95
Chitozan	0.095	1.463	0.97	0.145	1.454	0.98

The Freundlich constant k and n were determined 2/812 and 1/699 with correlation coefficient of 0/93 for modified bagas. Kamble et al (2007) used chitin and chitozan for adsorption of fluoride and determined Freundlich constants k and n equal to 0/34 and 0/7 for chitin and 1/27 and 0/897 for chitozan, respectively [20]. The higher k constant, the adsorption is more efficient. It can be seen that the k value constant is 2 orders of magnitude in the current study, compared to Kamble et al. The comparison of constants and linear equations of isotherms indicate that both Langmuir and Freundlich isotherms are well fitted (more than 0/95) with results for bagas, modified bagas and chitozan. The Langmuir model with correlation coefficient of 0/99 for modified bagas is more suitable than Freundlich isotherms.

4. Discussion

4.1 The effect of pH

Figure 1 shows that the most removal efficiency of fluoride was obtained in the pH range of 5-9, and the pH value of 7 was the best for all three adsorbents. In another study by Kamble et al (2007), which fluoride adsorption by chitosan and modified chitosan (modified by lanthanium) was investigated, the best removal efficiency was observed in the pH range of 5-9 by the most fluoride removal in the pH value of 6 [20]. But, in other studies by Wajima et al (2009) and Alagumuthu et al (2010) the most fluoride removal efficiencies were observed at the pH value of 3 [21-22]. They have used titanium hydroxide and zirconium as adsorbent. Tang et al (2009) proved that fluoride adsorption is highly pH dependent and the best results for fluoride adsorption by ferric hydroxide granules was achieved in the pH range of 3-6/5 [23]. In the current study, pH did not have an important effect on fluoride adsorption, so that the most removal difference in the pH range of 3-11 was only 10%. This finding is in accordance with Nigussie et al (2007) [8] and Sairam et al (2009) [14]. They also did not report any important effect of pH on adsorption efficiency in the pH range of 3-8 and 4-10 respectively. Biswas et al (2009) reported that fluoride adsorption in the pH range of 5-7/5 was constant [24]. These differences maybe mainly are due to different adsorbents and pollutant concentrations.

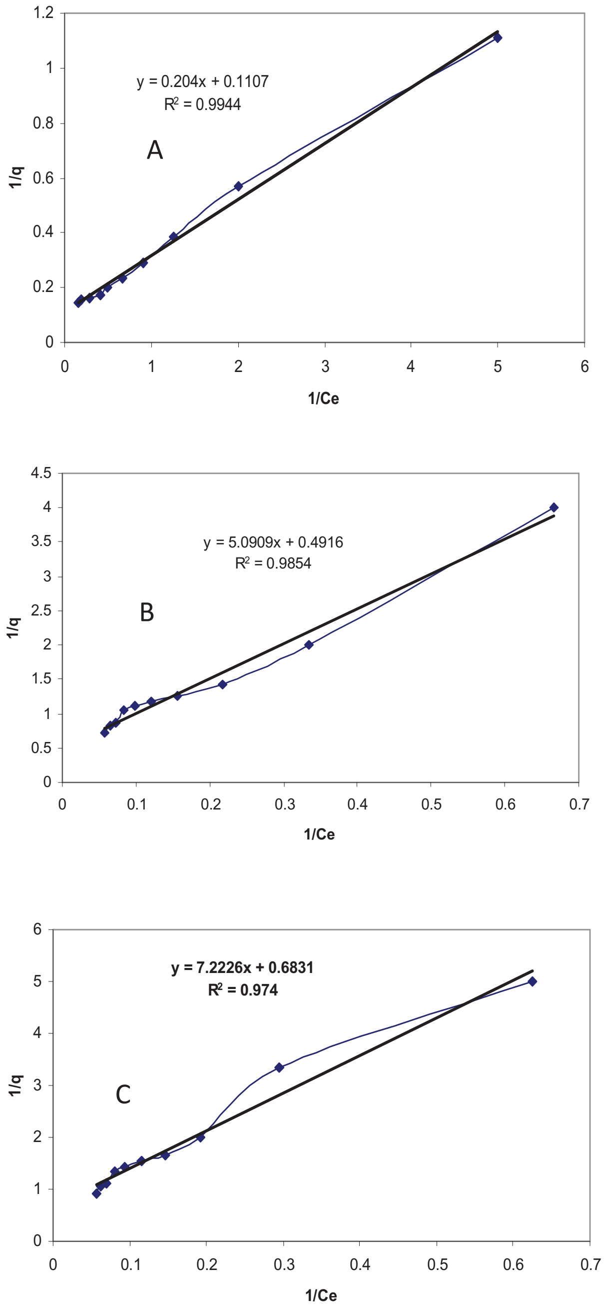

Figure 5: Langmuir isotherms of fluoride adsorption in optimum conditions: A) modified bagas, B) bagas, C) Chitozan

4.2 The effect of contact time

The effect of contact time on fluoride adsorption by chitozan, bagas and modified bagas is presented in figure 2. The fluoride adsorption in the first 30 min is rapid and then was slowed gradually. Kamble et al (2007) [20] and sairam et al (2009) et al [14] also reported that the fluoride adsorption is rapid in the first 30 min and is decreased in remaining time. According to removal efficiency after 60 min and no variation in results after this time, the time value of 60 min was determined as equilibrium time.

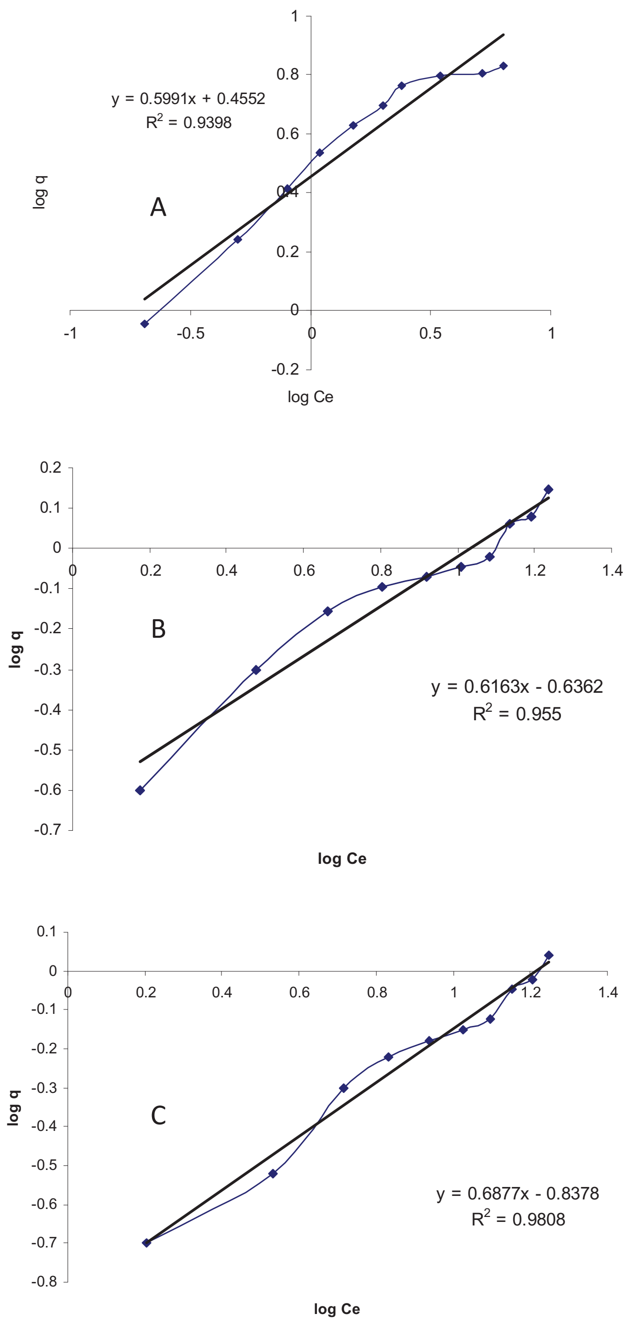

Figure 6: The Freundlich isotherm of fluoride adsorption in optimum conditions: A) modified bagas, B) bagas, C) Chitozan

Wajima et al (2009) also reported the time value of 60 min was determined as the equilibrium time [21]. Tang et al (2009) reported that the fluoride adsorption after 60 min contact time was about 70% and after 300 min was 95%. In the current study, 90% of removal was achieved after 45 min contact time and 95 % after 120 min. It should be mentioned that the fluoride adsorption did not vary significantly after 240 min contact time.

4.3 The effect of adsorbent dosage

The equilibrium concentration of fluoride decreased along with adsorbent dosage increase, so that variation of dosage from 1 to 5 g/L led to effluent fluoride concentrations of 0/9 to 0/25 mg/L, respectively. In other word, removal efficiency of 82% for adsorbent dosage of 1 g/L increased to 95% at adsorbent dosage of 5 g/L. These findings are in accordance with Nigussie et al (2007) which also reported the decrease of equilibrium concentration of fluoride along with adsorbent dosage increase. They have stated that adsorbent increase from 1 to 30 g/L led to improvement of removal efficiency from 45% to 95% and the adsorption capacity of 4/5 mg/g decreased to less than 0/5 mg/g [8]. In the current study, adsorbent increase from 1 to 5 g/L led to variation of adsorption capacity from 4/1 mg/g to 0/95 mg/g. Despite of only 5 orders of magnitude in adsorbent dosage, but adsorption capacity decreased to 25% of its initial value, which is a suitable result. In another study by Kamble et al (2007), adsorbent dosage variations from 1/5 to 20 g/L led to decrease of adsorption capacity from 3/1 mg/g to 0/4 mg/g [20]. Biswas et al (2009) reported that adsorbent increase from 2 to 16 g/L resulted to adsorption capacity variations of 4 mg/g to 1/5 mg/g. Considering the increase of adsorption capacity along with initial concentration of fluoride, the most adsorption capacity in the concentration ranges of this study (2 – 20 mg/L), was observed for the fluoride concentration of 20 mg/L by the value 6/8 mg/g modified bagas. The adsorption capacity for bagas and chitozan was 1/4 and 1/1 mg/g, respectively in the same conditions. The obtained results indicate that bagas is a suitable adsorbent for fluoride, provided that be modified with some chemicals. Modification of bagas as an adsorbent can improve the adsorption capacity to 6 orders of magnitude which is also more than similar studies. The fluoride adsorption capacity for chitozan has been equal to 0/052 mg/g in two different studies by Sairam and Viswanathan [8, 25]. Also, the fluoride removal efficiency by chitosan at the initial concentration of 5/35 mg/L was reported to be only 10% by Takre et al (2010) [26]. While in the present study, removal efficiency in the initial fluoride concentration of 5 mg/L for chitozan concentrations of 1 and 5 g/L has been 14% and 28%.

4.4 The effect initial fluoride concentration

The effect of initial fluoride concentration was determined when the other parameters were optimized. Along with initial fluoride concentration increase from 2 to 20 mg/L, the removal efficiency decreased from 90% to 68%. This finding is in accordance with Kamble et al (2007) report [20]. Generally, adsorption capacity increases directly with initial fluoride concentration, which can be due to fewer active sites. This leads to more fluoride penetration and activity [8].

5 Conclusion

The application of inexpensive adsorbents or agricultural and industrial wastes can be a suitable way for removal of environmental pollutants. In the current study, the application of chitozan, bagas and modified bagas for removal of fluoride from water was investigated. Chitozan and bagas did not show good capability for fluoride removal, but modified bagas with adsorption capacity of 6/8 mg/g is a suitable adsorbent for fluoride removal. Both Langmuir and Freundlich isotherms show good correlation for description of results, but the Langmuir model with the correlation value of 0/99 is superior. In the optimized conditions, including the pH value of 7, contact time of 60 min and adsorbent dosage of 2 g/L, more than 90% removal efficiency can be obtained for modified bagas.

According to results of this study, it can be concluded that adsorption process with modified bagas can be considered as an efficient, reliable, viable and cost effective method for removal of fluoride from water solutions. This adsorbent can reduce fluoride concentrations to less than 1/5 mg/L in optimum conditions, which is acceptable in more countries of the world.

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