Removal of Fluoride Ions from Wastewater Using Green and Blue-green Algae Biomass in a Fluidized Bed System

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ABSTRACT

The removal of fluoride ions from aqueous solution onto algal biomass as biosorbent in batch and continuous fluidized bed systems was studied. Batch system was used to study the effects of process parameters such as, pH (2-3.5), influent fluoride ions concentration (10- 50 mg/l), algal biomass dose (0–1.5 g/ 200 ml solution), to determine the best operating conditions. These conditions were pH=2.5, influent fluoride ions concentration= 10 mg/l, and algal biomass dose=3.5 mg/l. While, in continuous fluidized bed system, different operating conditions were used; flow rate (0.667- 0.800 l/min), bed depth (8-15 cm) corresponded to bed weight of (80- 150 g). The results show that the breakthrough time increases with the increase of bed depth but decreases with the increase of flow rate. Thomas and Yoon-Nelson models were used to analyze the experimental data and there was a good matching between the theoretical and the experimental data for both models. Desorption studies indicate that NaOH solutions at different pH values (8-10) were used to recover the fluoride ions sorbed onto the algal biomass. It is noteworthy that the desorption efficiency at pH =10 remains close to 95 % of the initial value of sorption capacity. So the desorption performance remains appreciable.

Keywords: Fluoride ions Fluidized bed, algal biomass, Thomas and Yoon-Nelson models.

أزالة ايونات الفلورمن مياه الفضلات بأستخدام كتلة الطحالب الخضراء والزرقاء في نظام انبوب التميع

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تتناول هذه الدراسة استخدام الطحالب كمادة مازة لإزالة أيونات الفلور من محلول مائي في نظامي دفع متقطع ومستمر بأستخدام انبوب تميع. في نظام الدفع المتقطع تمت دراسة تأثير عدة معاملات مثل الرقم الهيدروجيني (3.5-2)، تركيز ايونات الفلو (10- 50 ملغ / لتر)، كمية المادة المازة (0-10 غرام / 200 مل من المحلول)، ووجد بأن افضل ظروف تشغيلية هي الرقم الهيدروجيني=2.5 ، تركيز ايونات الفلور=10 ملغ/لتر،

كمية المادة المازة=3.5 غم/لتر. بينما في نظام انبوب التميع المستمر تم استخدام ظروف تشغيلية مختلفة حيث ان معدل الجريان (0.667 -0.800لتر / دقيقة)، وارتفاع الحشوة (8- 15 سم) وبوزن(80 - 150 غ) على التوالي. توضح هذه النتائج أن زمن الإختراق يزيد مع زيادة عمق الحشوة ولكن يتناقص مع زيادة معدل التدفق. تم استخدام موديلي ثوماس ويون ونيلسون لتحليل النتائج المختبرية وكان هناك توافق بين النتائج النظرية والعملية لكلا الموديلين. أما دراسة عكس الامتزاز تشير الى استخدام محلول NaOH ولقيم مختلفة من الرقم الهيدروجيني (9-10) لاستخلاص الفلور الممتز على الطحالب. ومن الملاحظ ان الحصول على افضل عكس الامتزاز وبكفاءة 95% يحصل عندما تكون قيمة الرقم الهيدروجيني= 10.

الكلمات الرئيسية: ايونات الفلور، انبوب التميع، كتلة الطحالب، موديل ثوماس وموديل يون- نيلسون

1. INTRODUCTION

Fluoride is a ubiquitous element present in earth's crust. It belongs to group 17 of the Periodic Table and it is the most electronegative of all elements. Fluoride is considered as valuable and extensively used in industry such as toothpastes, fertilizers, production of graphite, semiconductors, electrolysis of alumina ,**Tripathy et al., 2006.** Large quantities of wastewater, which contains high concentrations of fluoride and its compounds, are generated from these activities. Fluoride may enters food chains and reaches to the human through either drinking water or eating plants and cereals. Fluoride has gained importance due to its dual influences on human beings. When present within the permissible limit, fluoride is an essential nutrient for the calcification of dental enamel and maintenance of healthy bones, so that it is purposely added to drinking water in small quantities to prevent dental caries. But the high concentration of fluoride is a serious hazard to human health and may causes fluorosis, brittle of bones, curvature of bones, dwarfishness, mental derangements, cancer, and in extreme cases even death. The permissible limit of fluoride in drinking water is 1 mg/l as recommended by WHO standards , **Meenakshi, 2006**. Pollution by fluoride has been observed in some natural water systems in Asia, Africa, America, and Europe, where the fluoride concentration can range from 0.01 to 3 mg/l in fresh water and 1 to 35 mg/l in ground water , **Rajiv Gandhi, 1993**. Due to high toxicity of fluoride to mankind, there is an urgent need to search for advanced wastewater treatment mechanisms to treat fluoride-contaminated water and to make it safe for human consumption. As a result, numerous efforts have been undertaken to find effective and low cost methods to remove fluoride from waste solutions.

Available treatments process for Fluoride from water and wastewater include chemical precipitation (by alum, lime, lime and alum and calcium chloride), adsorption (by activated alumina, clay and flay ash), ion exchange (by synthetic resins) and membrane technologies (by reverse osmosis and electro-dialysis). These methods require more technical support for operation and maintenance and the capital investment cost is very high ,**Mann and Mandal, 2014**. This is an obvious constraint on the use of these methods in certain applications, especially for fluoride removal from wastewater. Alternatively, the so-called biosorption, i.e., the property of certain dead biomass to bind and concentrate selected ions or other molecules from aqueous solution, could be considered. Biosorption by dead biomass is passive and based mainly on the affinity between the biosorbent and sorbate ,**Volesky, 2007; Sulaymon et al., 2012**. Different materials have been reported in the literature as inexpensive sorbents for fluoride removal; for example, crashed limestone **, Nath and Dutta, 2010.** Alum- , **Tripathy et al., 2006**. Rice husk ,**Vardhan and Karthikeyan, 2011**. Moreover, **Sulaymon et al., 2013a.** mentioned that biosorption by algae is proven to be quite effective at removing metal ions from contaminated solutions in a low-cost and environment-friendly manner. This can be attributed to the abandons of algal biomass and it has many negative charge active groups on its surface cell wall such as hydroxyl, carboxyl, amino, sulfhydryl, and sulfonate. These groups were part of the algal cell wall structural polymers, namely, polysaccharides (alginic acid, sulfated polysaccharides), proteins, and peptidoglycans. Although much of the current biosorption researches using algae are oriented towards the removal of metal cations, the binding of anions like fluoride to this biomass is a growing area of study. As well as, a few studies were carried out in continuous system using fluidized bed applications.

For evaluating the feasibility and effectiveness of biosorption in wastewater treatment it is essential to make predictions of the sorption performance, e.g. for facilitating process design. Therefore it is important to develop appropriate mathematical models of biosorption binding equilibrium and dynamic which are necessary as a prerequisite for all further work involving; batch, and column applications.

This work investigates the removal of fluoride in a fluidized-bed reactor of algal biomass as biosorbent. The preparation, characterization and sorption properties of biosorbent were reported. Moreover, the effect of some experimental conditions on the fluoride removal such as superficial velocity and bed height was evaluated and to model the process using a well-known empirical models.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1Collection of Biosorbent Material

Fresh samples of green and blue-green algae were used in this study as a biosorbent. This material was collected from the artificial irrigation canal in Baghdad University, Iraq. It was mainly combined of three species of algae. Blue-green Oscillatoria princeps alga was the highest percentage (88%), green Spirogyra aequinoctialis alga was (9%), and blue-green Oscillatoria subbrevis alga (3%). And to make it used friendly the collected algae were not separated. The foreign matters were removed manually from the collected algae, then rinsed with tap and distilled water to remove dirt, sands, and external salts. Afterward, the washed algae were kept in air for evaporating of water and dried in an oven at 65 °C for 48 h. The dried biomass were roughly chopped, grounded into powder, sieved, and kept in air-tight polyethylene container at room temperature. An average size of 0.55 mm was used for biosorption experiments with required amounts.

2.1.2 Fluoride Solution

All the chemicals used in this study were of analytical grade, and deionized water was used for solution preparation. A stock solution (1000 mg/l) of fluoride ions was prepared by dissolving appropriate amount of sodium fluoride (provided by Merck, Germany) in distilled water and stored in glass container at room temperature. The working fluoride ions solutions were prepared by appropriate dilution in accurate proportions of the stock solution immediately prior to use. The pH of the working solution was adjusted by using dilute HCl or NaOH solutions using a pH meter (type WTW, InoLab 720, Germany). Prior the experiments, all the glassware used for dilution, storage, and experimentation were cleaned with detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO_3 solution, and finally rinsed with distilled water before use.

2.2Methods

2.2.1 Batch System Experiments

Experimental parameters affecting the biosorption process such as pH (2-3.5), precipitant dose (0-1.5 g/ 200 ml solution), and initial fluoride ions concentrations (0-50 mg/l) were studied in batch system. The experiments were conducted in 250 ml stoppered conical flasks containing 100 ml of pre-determined fluoride ions aqueous solution (1–50 mg/l) and 1 g of algae, under constant shaking at room temperature (20 ± 3°C). The pH solution was adjusted to the desired value. The flasks were placed in a shaker (Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany) under constant shaking speed (200 rpm) for 3 h. After equilibrium biosorption, the sorbent was separated from aqueous solution by using filter paper (Whatman, No.42, diameter 7 cm) and the residual concentration of fluoride was measured. The concentration of fluoride in both initial and withdrawn samples was determined using Orion Multiparameter Kit Ion Meter. The instrument was calibrated each time the analysis was done. All the samples were measured in triplicate and the average value was obtained. The fluoride removal was calculated by using the following equation:

$$\text{Fluoride removal}=\left(\frac{C_o-C_e}{C_o}\right) \qquad \ldots\ldots\ldots\ldots\ldots..(1)$$

Where, C_o and C_e are the initial and equilibrium fluoride concentrations in water (mg/l), respectively.

2.2.2. Continuous system experiments

A fluidized bed reactor which is shown in **Fig. 1** was designed to investigate the algal biomass biosorption efficiency for fluoride ions. The fluidized bed reactor is a 7.5 cm inner diameter and 1 m high glass column. In order to homogenize and evenly distribute the liquid flow before it reaches the algal biomass bed section, the column consists of a calming entry section of length of 5 cm filled with glass beads of mean radius 2 mm and covered with stainless steel sieve. In addition, the fluidized bed reactor has a screen at the bottom to support the algal biomass particles and at the top to remove the presence of particles in the effluent. A 10 W lamp was installed behind the reactor to measure the expanded height of algal biomass bed accurately. The fluoride solution of 10 mg/l was pumped into the reactor vertically and fluidized the algal biomass bed at a flow rate of 40 l/h with the temperature kept at room temperature, that is, about 25±3 °C. The solution pH was adjusted to a desired value by using 0.1N NaOH / HNO_3. Samples were periodically taken from the effluent of the reactor at different time intervals and analyzed for fluoride concentration. The operation of the column was stopped when the outlet fluoride ion concentration reached its initial concentration.

The experimental sorption capacity can be obtained using equation 2; it is calculated from the area above the breakthrough curve, taking into account the volume of treated water through the column and the mass of biosorbent, used in the packed column.

$$q_{exp} = \int_{0}^{V_{total}} \frac{(C_0 - C_t)}{m} dV \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

Where, q_{exp} is the sorption capacity (mg/g); C_t is the withdrawn fluoride concentration (mg/l); m is the mass of the algal biomass (g), V (l) is the volume of treated water (**Meenakshi, 2006**).

2.2.3 Breakthrough Curves Models

There are many dynamic models for describing the performance of column systems. Thomas model is widely used for its simplicity and for its adequate accuracy in predicting breakthrough curves under various operating conditions. The model is represented by the following equation (**Yilmaz-Ipek, 2013**):

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{K_T(q_T m - C_0 V)}{Q}\right]} \qquad \ldots\ldots\ldots\ldots\ldots. (3)$$

Where, K_T is the Thomas rate constant (l/min.mg), m is the mass of sorbent (g), Q is the volumetric flow rate (l/min), C is the sorbate concentration and q_T is the Thomas sorption capacity (mg/g).

The Yoon-Nelson model is a simple model for describing the sorption and breakthrough curves of the sorbate. It requires no detailed data on the characteristics of the sorbate, the type of sorbent, or the physical properties of the sorption bed, and is expressed as follows (**Yilmaz-Ipek, 2013**):

$$\frac{C}{C_o} = \frac{\exp(K_{YN} t - \tau K_{YN})}{1 + \exp(K_{YN} t - \tau K_{YN})} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where τ is the time required for 50% sorbate breakthrough (min) when fluoride concentration C (mg/L) is one half of C_o, and K_{YN} is the rate constant.

2.2.4 Desorption

When the relative concentration (*C/Co*) achieved a value near about 1, the adsorption process become saturated and regeneration process was start to wash out the loaded metal ions from the pores of the adsorbent. Desorption is a very important concern to reuse the biosorbent and reduce process costs. It is desired that the adsorbent should be close to its original form, and should not lost its sorption ability after desorption. In addition, the recovery of valuable metals from dilute aqueous wastes is a complementary process. For this case, acidic or basic solutions are frequently used for desorption of metal ions sorbed on different sorbents (**Sezen et al., 2012**).

3. RESULTS AND DISCUSSIONS

3.1Characterization of the Algal Biomass

A sample of powdered algal biomass was analyzed for surface characterization such as surface area and porosity. **Table 1** listed the physicochemical properties of the algal biomass used in this study. The surface area of algal biomass was determined from nitrogen adsorption-desorption isotherm analysis using a Micrometrics Nano Porosity System.

It can be seen that the surface area and the pore volume of the biosorbent were 4.07 m^2/g and 0.713 cm^3/g, respectively. These values are small compared with those of other materials like activated carbon, so that the removal efficiency is very sensitive to the porous sorption. In this case it is recommended to use fluidized bed reactor rather than fixed bed system.

3.2 Parameters Affect Biosorption

Fig. 2 depicts the fluoride ions removal as a function of algal biomass dosage for different initial concentrations. Clearly, the fluoride ions removal increased with the increase of algal biomass dose from 0.01 to 0.7 mg/200 ml solution and thus the biosorbent dose was an important factor to the fluoride ions removal. The reason being that; an increase in the sorbent quantity in the aqueous solution results in a larger exchangeable area for fluoride ions biosorption. This figure also shows that the removal rate of fluoride ions considerably remains stable at algal biomass dosages beyond 0.7 g/200 ml aqueous solution, implying that the best amount of algal biomass is 3.5 g/l solution for all initial fluoride ions concentration values. Therefore, this dose is used in all subsequent experiments. Moreover, experimental results revealed that the highest fluoride ions removals were 0.93, 0.88, and 0.68 at initial concentrations of 10, 20, and 50 mg/l, respectively. By increasing the initial concentration from 10 to 20 mg/l the removal efficiency does not alter greatly. This is probably can be inferred due to the fact that the amount of algal biomass used in this experiment contains enough sorption active groups and sites for the binding of fluoride ions. When the initial concentration increased to 50 mg/l the removal of fluoride ions was significantly affected. This can be attributed to the increase in the fluoride ions concentration provides a greater driving force to overcome the mass transfer resistance through particles as well as the collision between fluoride ions and algal biomass particles is enhanced at higher concentrations as stated by , **Hekmatzadeh et al., 2013**. However, increasing the initial fluoride ions concentration led to a drop in the removal of it as shown in **Fig. 2**.

The most important factor affecting the sorption of ions is the pH of the aqueous solution. According to , **Cengeloglu, 2002.** the removal of fluoride ions is highly efficient under low pH values this is due to positive charge ions (H^+) density on the sites of biomass surface will enhance metal anion sorption. Hence, the pH was initially adjusted between 2 and 3.5 and the results are depicted in **Fig. 3**. At initial pH 3 the final pH slightly increased to 4.5. This can be explained by that untreated algae biomass generally contains light metals such as K^+, Na^+, Ca^{2+}, and Mg^{2+} which are originally present in freshwater. These ions are bound to the surface acidic functional groups and when algal biomass reacts with metal-bearing solution, releases light metal ions and pH increases, these results agreed with , **Sulaymon et al., 2013b**. This also was explained in terms of ion exchange, whereby the observed released light metals balanced the uptake of cation ions as stated by ,**Schiwer and Volesky, 1996; Kratochvil, 1997**. It is clear from **Fig. 3** that the solution pH value was an important parameter controlling the biosorption of fluoride ions onto the surface of the algae biomass. From pH 2.0 to 2.5, biosorption of fluoride ions onto algal biomass showed increasing phenomena and at pH 2.5 it attains the maximum removal. The increase in fluoride ions removal with the increase in pH is because at acidic solution, more protons will be available to protonate the active group and increasing the number of binding sites for biosorption of fluoride ions. These results agreed with **, Elwakeel, et al., 2014**.

Above pH 2.5, the biosorption of fluoride was decreased sharply. This trend can be attributed to that at pH above 2.5 the surface of algal biomass does not adequately protonated with a positive charge and fluoride ions could thus be bound. So at $pH < pH_{PZC}$ (PZC is the point of zero charge) the surface of the sorbent is positively charged, indicating a greater affinity for anions as stated by ,**Zelmanov and Semiat,**

2014. These results are in agreement with, **Roberts 1992, Kratochvil and Volesky (1998)** who pointed that for anionic metals only when the solution pH is lower than the conjugated acid dissociation constant pKa value, the active groups such as carboxylic and chitin amide groups could be effectively protonated with a positive charge and an anion metal could thus be bound. At pH below 2.5 and despite of high density of H^+ ions, the fluoride ions removal was decreased owing to the dissociation of the biosobent as stated by , **Sulaymon et al., 2014**. For the further experiments the pH solution was fixed at 2.5.

3.3 Fluidized Bed System

Breakthrough curves generally permit a good description of the processes in sorption columns. The resulting breakthrough curves at different parameters are presented in **Figs. 4-7**. The experimental biosorption capacity values of the fluidized bed reactor are shown in **Table 2**. It can be seen that Thomas and Yoon-Nelson models show a good fit with the experimental data related to R^2 values. **Figs. 4 and 5** show the breakthrough curves of algal biomass towards fluoride ions at different flow rates (0.667, 0.734, and 0.800 l/min) and an expanded bed height of 10 cm for the two models. The breakthrough generally occurred faster with higher flow rate and the slope of the breakthrough curve increased with increasing liquid flow rate. The breakthrough points (90% removal efficiency) occurred at 2, 9 and 20 min for liquid flow rate of 0.800, 0.734, and 0.667 l/min, respectively. This can be attributed to that increasing the flow velocity would decrease the contact time between the fluoride molecules and algal biomass particles along the column bed. Increasing the flow rate may be expected to make reduction of the liquid film thickness. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate as well as there is not enough time for sorption equilibrium to be reached. In addition, decreasing the flow rate allows the solute to diffuse more efficiently in the sorbent: the mass transfer zone (where the reaction takes place) is shortened. These mechanisms are also consistent with that obtained by , **Sulaymon et al., 2010**. The maximum biosorption capacities of the fluidized bed reactor at different flow rates are 2.94, 2.53 and 2.1 mg/g for flow rate 0.667, 0.734, and 0.800 l/min, respectively.

The effect of bed depth on the sorption process was investigated at bed height of 8, 10 and 15 cm (corresponded to bed weight of 80, 100 and 150 g). Thomas and Yoon -

Nelson models were used to predict the breakthrough curves. The two models show a good fit with the experimental data and the results are depicted in **Figs. 6 and 7**. These results showed that with increasing the bed weight of the algal biomass the time at which an effluent concentration reached breakthrough point is increased, this is due to the large contact time between the fluoride ions and biomass particles at a high bed depth. Smaller bed heights will be saturated in less time. Also, an increase in the bed depth will increase the surface area for the sorption which will improve the removal efficiency. The results agree with that obtained by ,**Sulaymon, and Ebrahim, 2010**.

3.4 Desorption process

In the present study, NaOH solutions at different pH were used to recover the fluoride ions sorbed on the algal biomass. This strong base will displace the sorption equilibrium toward fluoride ions release. The desorption capacity values of the column are shown in **Table 3**. The volume of dilute NaOH solution required to recover the fluoride for each desorption cycle was fixed at 10 l. It is noteworthy that the desorption efficiency at pH equal 10 remains close to 95 % of the initial value of sorption capacity. So the desorption performance remains appreciable.

4. CONCLUSIONS

Algal biomass was used to remove fluoride ions from aqueous solution in continuous fluidized column system and it was found to be very effective adsorbent. The present work demonstrates that the operation is highly dependent on the pH, influent fluoride ions concentration, and algal biomass dose. The breakthrough time in continuous fluidized bed system was increased with the increase of bed depth but decrease with the increase of flow rate. The experimental data were well fitted to Thomas and Yoon-Nelson mathematical models. From the mathematical models it was observed that the maximum metal uptake capacity was decreased with the increase of bed depth but increased with the increase of flow rate. Desorption process shows that the algal biomass is economically suitable for the regenerate 95 % of the initial value of sorption capacity of fluoride ions at pH =10.

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Table 1. Properties of the algal biomass used in biosorption experiments.

Parameter	Value
Particle diameter (mm)	0.4-0.6
Bulk density(g/cm^3)	0.680
Real density (g/cm^3)	1.100
Surface area (m^2/g)	4.07
Micropore volume (cm^3/g)	0.713
Bed void fraction	0.577
Point of zero charge, pH$_{PZC}$	5.5
Total exchange capacity (mEq/g)	1.24

Table 2. Experimental and theoretical parameters in fluidized bed reactor for Fluoride removal.

Run	Experimental Parameters						Thomas model parameters			Yoon and Nelson model parameters		
	Q (l/min.)	pH	m (g)	h (cm)	C_o (mg/l)	q (mg/g)	K_T (l/min.mg)	q_T (mg/g)	R^2	K_{YN}	τ	R^2
1	0.667	2.5	100	10±0.1	10	2.940	$9.98*10^3$	2.794	0.998	0.099	41.889	0.997
2	0.734	2.5	100	12±0.1	10	2.530	$9.50*10^3$	2.400	0.998	0.095	32.987	0.998
3	0.800	2.5	100	14±0.1	10	2.100	$9.68*10^3$	1.997	0.995	0.096	24.957	0.995
4	0.667	2.5	150	15±0.1	10	2.992	$8.54*10^3$	2.88	0.999	0.085	58.073	0.999
5	0.667	2.5	80	8±0.1	10	1.52	$9.55*10^3$	2.775	0.998	0.095	33.291	0.998

Table 3.Desorption capacity values

Run	Experimental Parameters					
	Q (l/min.)	pH	m (g)	h (cm)	C_o (mg/l)	q (mg/g)
1	0.667	8	100	10±0.1	10	2.107
2	0.667	9	100	10±0.1	10	2.556
3	0.667	10	100	10±0.1	10	2.799

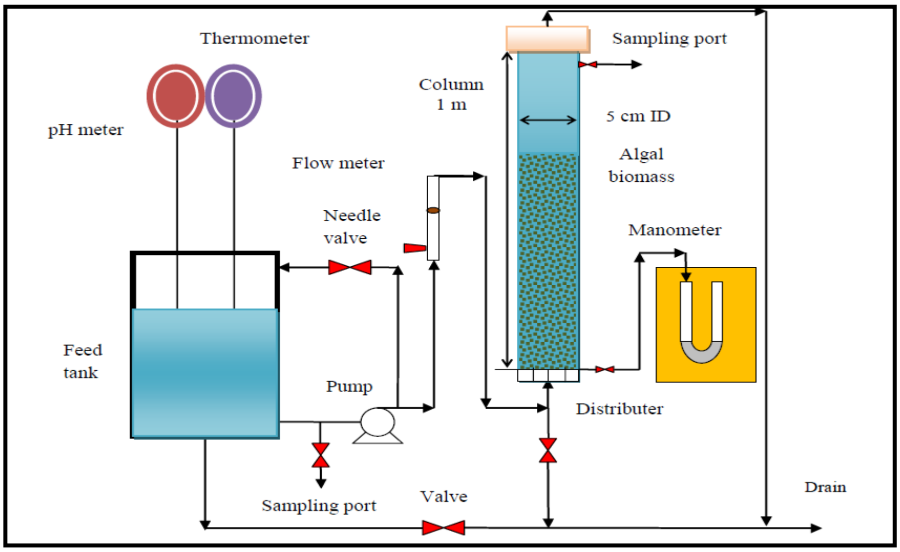

Figure 1. Experimental fluidized bed setup, A: Metal solution tank, B: Pump, C: Flow meter, D: Distributer, E: Column reactor.

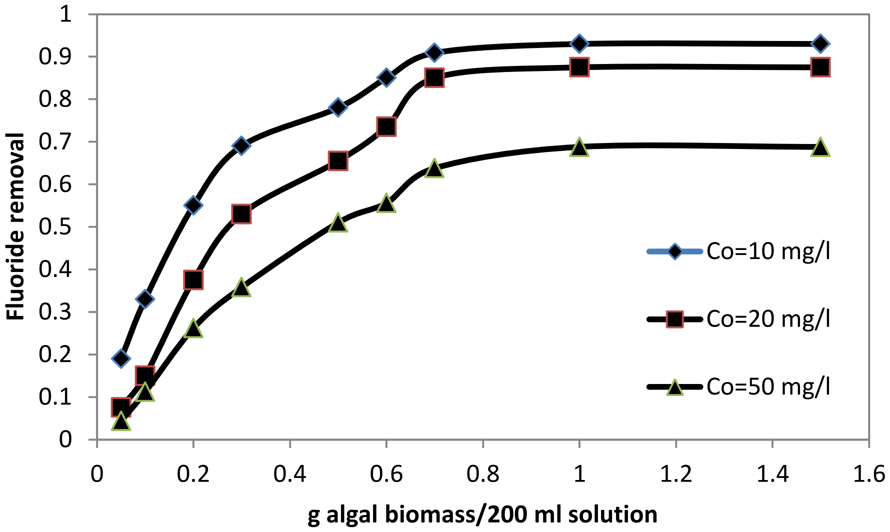

Figure 2. Effect of algal biomass dosage and initial concentration on removal of fluoride from aqueous solution, pH 2.5, at room temperature, contact time: 4 h at 200 rpm.

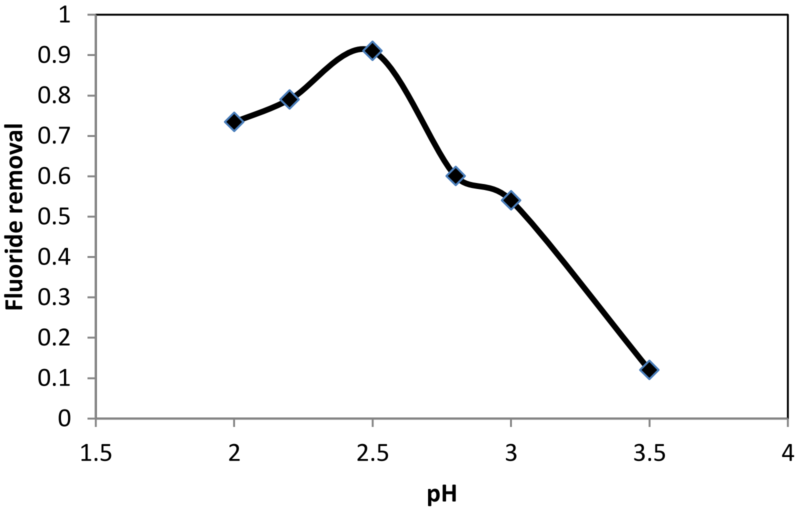

Figure 3. Effect of pH on removal of fluoride from aqueous solution at room temperature, 200 g algal biomass/200 ml, contact time: 4 h at 200 rpm.

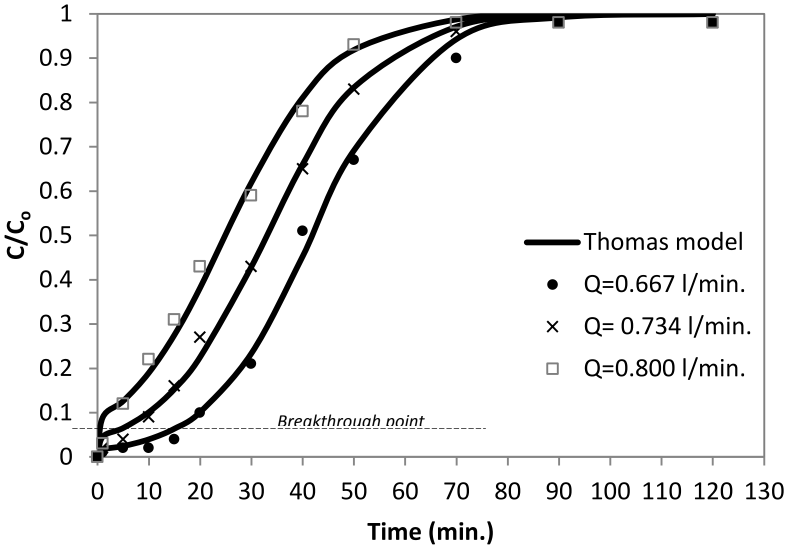

Figure 4. Effect of flow rate on fluoride removal in fluidized bed reactor at pH=2.5, Co=10mg/l, biomass weight =100g using Thomas Model.

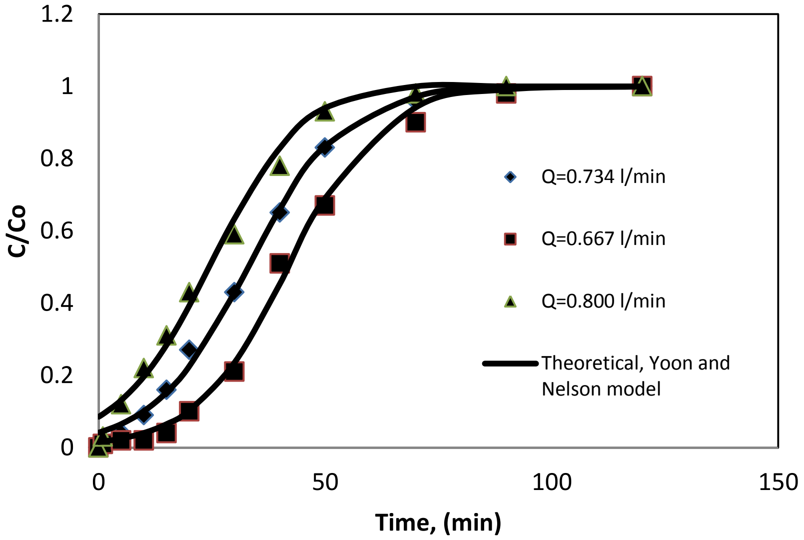

Figure 5. Effect of flow rate on fluoride removal in fluidized bed reactor at pH=2.5, Co=10mg/l, biomass weight =100g using Yoon and Nelson Model.

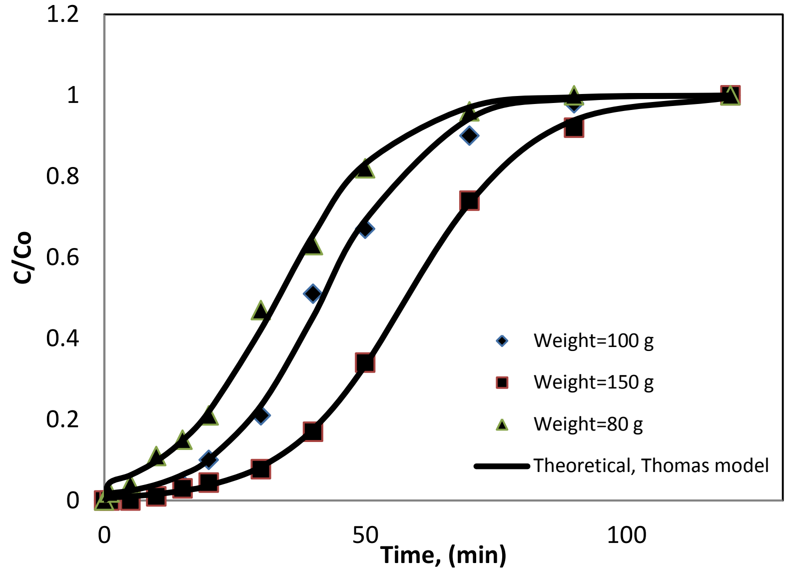

Figure 6. Effect of algal biomass weight on fluoride removal in fluidized bed reactor at pH=2.5, Co=10mg/l, flow rate =0.667 l/min using Thomas Model.

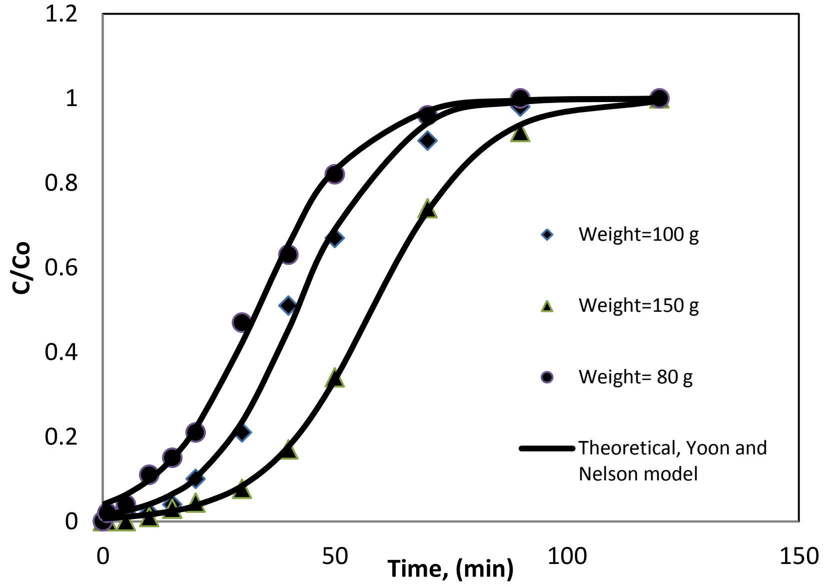

Figure 7. Effect of algal biomass weight on fluoride removal in fluidized bed reactor at pH=2.5, Co=10mg/l, flow rate =0.667 l/min using Yoon and Nelson Model.