REMOVAL OF FLUORIDE FROM SHATT AL-ARAB DRINKING WATER USING A NOVEL LOW COST MATERIAL

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ABSTRACT

Drinking water contamination by fluoride component (F-) is considered as a main public problem in Basra city. The current study highlights on the removal of (F-) from drinking water using effective and low cost materials namely, banana shell and new technical that prepared from orange shell loaded with Zirconyl chloride solutions (Z-r4 (O-H)8 (H2-O)16] C18 (H2-O)12) to develop active adsorption sites for fluoride. High removal efficiency of 94.4 was achieved using fixed bed column loaded (Zc-dejr) under optimum operating conditions, 15.1 ppm of feed concentration, 4.5 pH of feed solution and 4 cm of bed depth. Result of breakthrough profile showed that Thomas was coincided well with the experimental data. Two model, Pseude first order and Pseudo second order where used for finding the mechanism of adsorption kinetics for fluoride (F-) removal by two-bio adsorbents. The result showed that the external adsorption besides to the intra-particle diffusion contributes to the rate influential step. Lagmaier model gives the better result model for the two adsorbents then Temkin isotherm model (TIM). The final concentration of fluoride in treated water with the banana shell absorbent was 1 mg/l, and with the new solution (Z-r4 (O-H)8(H2-O)16 ) C18 (H2-O)12 ) was 0.5 mg /l which is acceptable with the standard World Health Organization (WHO).

KEYWORDS: Fluoride Removal; Low Adsorbent; Drinking Water; Isothermal Model; Intra-particle diffusion.
1. INTRODUCTION
Fluoride is important as well as toxic for the human health. Its higher concentration in water creates health problems. Although, high concentration of fluoride (F-) let to decrease the coliseum, protein and vitamins in the body (Waghmare and Arfin, 2015; and Chiou and Ku, 2011) and also principals to generate various diseases like arthritis, brittle bones, cancer, osteoporosis, infertility, brain damage, and thyroidisorder (Li, et al., 2011; and Deng and and Saha, 2010). About two million of people in the world are influenced by the dental fluorosis which is resulted from wastewater outlets of most industrial process, some of these process the superphosphate fertilizer (Abou-Elela and El-Kamah, 1995; and Mohammad aand Marwan, 2014) glas/s and ceramic industrial processes (Kae, et al., 2016; and Falone and Bernardo, 2013), (Al) and ZN (Zhijie and Mingfeng, 2011; and Cui and Qian, 2011). The World Health Society has quantified 1.5 mg/L of fluoride (F-) concentration as the acceptable range in drinking water. Concentrations above this value carry an increasing risk of dental fluorosis, and much higher concentrations lead to skeletal fluorosis. The value is higher than that recommended for artificial fluoridation of water supplies, which is usually 0.5–1.0 mg/l. In Iraq, the maximum allowable limit of fluoride is 1.5 mg/l based on the World Health Society. There are various knowledge were developed to decreased fluoride (F-) content in water, such as thickening and electrodialysis (Srivastava et al., 2013; and Hu and Dickson, 2006), membrane operation and electrodialysis (Arda and Orhan, 2009; Dominguez and Charbit, 2005; Sunil, 2013; and Dickson and Hu, 2006) electrochemical treatments (Mokashi and Parlkar, 2013; Maallemi, et al., 2008; Erguna and Tora, 2008), ion-exchange and its variation (Ruxi and Hong, 2002; and Grames, 2002), moreover, the adsorption technique is the actual method for eliminating fluoride from drinking water. Recently, most of researcher targeted on fluoride (F-) removal using normal, biomass component and synthetic material such, fly ash (Piekos and Palawanska, 1999), activated alumina (Ghorai, and K., 2005), chitosan drops (Labhsetwar, et al., 2010) and red sludge (Ranjeeta and Shikha, 2013). The last study for fluoride removal has been used low cost materiel of bone char for fluoride removal (Sorlina, 2011). The present work was focused on great an economical method for high removal of fluoride by low cost adsorbent, banana shell and an orange shell remain after its loaded with Zirconyl chloride solution named as (Zc-dejr). Zirconyl chloride solution has high selectivity to fluoride over other comparable anionic species. It also has high reusability of up to several continuous sequences of adsorption followed by desorption negligible degradation of the adsorption capacity. Additionally, an orange shell remain is considered as disposal metal from any user and have low cost because its feed material is orange waste itself, one of the plentiful agricultural biomass, and
environmentally benign and rich in pectic acid, on which high content of Zirconyl chloride solutions that effectively adsorbed as active anion exchanger. According to the above results, this research aimed to (1) investigate a fluoride ion removal in drinking water using a fixed bed column packed with a novel adsorbent orange shell loaded with Zirconyl chloride.

2. METHODS

2.1. Chemicals and instruments

The analytical component zirconyl chloride octahydrate, \( \left( \text{Zr}_4 (\text{O-H})_8 (\text{H}_2\text{O})_{16}\right) \text{C}_{18}^+ (\text{H}_2\text{O})_{12}^- \) was obtained from Wako Chemical Co. Ltd., China. Stock solution was equipped by melting 2.10 g of fluoride sodium (FNA) in 1000 ml of purified solvent (pure H\(_2\)O). The pH of the solution was kept constant by adding half molarity of hydroxide sodium in (mole per liter). The fluoride concentration (ppm) was measured by using ion chromatography (Dionex model ICS: 1500).

2.2. Adsorbent preparation

2.2.1. Orange preparation

An orange shell waste was collected from local shops in the Basra city, Iraq. Before the experiments operation, the dehydrated orange juice waste was splashed twice with fresh water to eliminate inquisitive biological compounds such as sugar, 2-hydroxypropane, 1, 2, 3-tricarboxylic acid, limonene, chlorophyll and other compounds. Then, it is dried at 75°C overnight and stored for metal uptake experiments. The washing dehydrated orange juice waste was grounded into smaller bits and analyzed using sieve analysis to obtain required particle size (75–125 µm). The adsorbent for fluoride removal was prepared from dehydrated orange juice remains supplied from JA Beverage Saga Co. Ltd., Japan, by loading zirconyl chloride octahydrate solution onto its polymer matrix according to the method described in Paudyal et al., 2013. The dehydrated orange juice remains was immersed with further zirconyl chloride octahydrate solution for formation the active locations for fluoride ion (Scheme 1). Four gram of dehydrated orange juice remains was filled in 1 liter conical flask along with 500 ml of 0.1m of \( \left( \text{Zr}_4- (\text{O-H})_8 (\text{H}_2\text{O})_{16}\right)\text{Cl}_{18}(\text{H}_2 = \text{O})_{12}^- \) solution and the mixture was then stirred for 1 day at 25, 35, 40 and 50°C to formulate different types of adsorbents for fluoride removal. After the all-time of mixing mixture, each sample was filtered, washed with distilled water many times to remove un-adsorbed Zirconium ion from the balm out layer and dried at 75°C.
2.2.2. Banana shell preparation
Banana shells are equipped from the local shop of banana. A banana shell waste was collected from local shops in the Basra city. Before the experiments operation, it was washed with distilled, water three times to remove the dust. Then, it is dehydrated initially for 48 hr, later in the burning air oven at 100°C for 36 hr. Dehydrated banana shells were rumpled in a grinder, and then it was sieved using sieve analysis (ASTM mesh of 510 μm). Final mixture is mixed with 0.1 M of HCl for 24 h. After the mixing, the mixture is washed several times to create it neutral, and then dried in hot air for 1 day.

2.3. Batch and fixed-bed column experiments
The effects of physicochemical operating parameters for the fluoride column absorption were investigated using batch experiments. Butch operation studies were carried out using conical flasks of 250 ml that placed in water bath, shocked at 360 rpm. After that, all samples were sieved using filter paper and then analyzed using SPADNS method. The required initial fluoride concentration (about 20 mg/l) was equipped from stock solution which prepared by dissolving 250 mg of fluoride sodium (100 mg/l) for each liter of purified water. In the fixed-bed column experiment, the columns were made from glass tubes of 0.5 m total length and 0.01 m of interior diameter. The dehydrated orange juice remains with zirconyl chloride octahydrate solution was first wetted with distilled water. The wetted adsorbent was then packed into a column as follows. First, the column was packed with glass drop about 10 cm followed by a cotton layer about 4 cm and then wetted mixture was packed with (3–8 cm) height. The packed column was filled with 4 cm cotton layer and 10 cm glass drop again to prevent any fluctuating during the operation. Effluent samples were collected using a Bio-Rad model-2110 automatic fraction collector. After 95 percent of the bed capacity was exhausted, the column operation will be completed. The feed solution temperature was fixed at 27°C using thermostatic bath.

3. MODELING STUDY
3.1. Predicting of breakthrough curves using Thomas model
The dynamic response of fixed column and the influence of operation parameters was investigated using breakthrough profile, which give a good feature for absorption response. The breakthrough profile is commonly stated in terms of adsorbed component concentration or regularized concentration defined as the ratio of effluent to inlet concentration as a function of time. From the breakthrough appearance time (t₁) and terminated time (t₂), the mass transfer zone (dt) and the adsorption capacity were calculated using equations below, respectively.
\[ \text{dt} = t_2 - t_1 \]
\[ q_{aps} = \frac{(C_0 - C_e)V}{w} \]

Where: \( q_{aps} \), the equilibrium uptake capacity in (mg/ g); \( C_0 \) and \( C_e \) are initial and final fluoride concentrations respectively; \( V \), is the volume in (Liter); and \( w \), the dry mass of component used as the adsorbent in g.

### 3.2. Isothermal Model

Two models were used for the adsorption characteristics Temkin (TM) and Langmuir models (LM), which are presented in linearized form (Chen and Wu, 2004):

(TM) formula is given as:

\[ q_{aps} = [R \cdot \frac{T}{b} \cdot \ln a] + [(R \cdot T) \cdot \ln C_e] \]

Where a, b are the adsorption constants, \( C_e \) equilibrium concentration (mg/l) and R is the constant;

The linearized Langmuir equation (LGM) is given as (Chen and Wu, 2004):

\[ \frac{C_0}{q_{aps}} = \frac{C_e}{q_{max}} + \frac{1}{b \cdot q_{max}} \]

Where: \( q_{max} \) (mg/g) is the higher value capacity; b is the adsorption attraction coefficient in (l/ mg) which represent the slope of the adsorption equation.

### 3.3. Adsorption kinetics model

Two models were performed to study the kinetics of adsorption fluoride on banana shell and the dehydrated orange juice waste as follow below:

Pseudo-first order model (PFM st):

\[ \text{LOG} \left[ q_{abs} - q_t \right] = \log \left[ q_e - 0.434 \cdot K_1 \cdot t \right] \]

Pseudo-second-order model (PSM nd)

\[ t \cdot q_t^{-1} = t \cdot q_{abs}^{-1} + \left( 1 - k_2^{-1} \cdot q_{abs}^{-2} \right) \]

Where: \( q_t \) is the amount of adsorbed at different period in (mg/l); \( K_1 \) in (min \(^{-1}\)) and \( K_2 \) are the kinetics rate constants for (PFM st) and (PSM nd), respectively.

### 4. RESULTS AND DISSECTION

#### 4.1. Results of isothermal Model

Fig. 1 shows a linear plot of the Temkin isotherm model (TIM) for the two different absorbents. All the adsorption parameters (a and b) for these adsorbents were calculated from the linear
plots of models. Fig. 2 shows the Langmuir isothermal model plot for different adsorbent. The maximum adsorption parameters in (mg/g) and adsorption attraction coefficient (b) for the two adsorbents are calculated by comparing the line slope value and intercept (1/b, qmax) with Fig. 2 where the result is tabulated in Table 1. Table 1 showed that the correlation coefficients (R2) values are higher 0.98 for Langmuir model. Therefore, LG model gives the better result model for the two adsorbents then Temkin isotherm model (TIM). It illustrated that, a maximum adsorption capability for dehydrated orange juice remains adsorbent is greater then Banana shell. It indicates that the experimental data was close fitting with Langmiur isotherm model (LIM).

Fig. (3a and b) shows kinetics results of two models, Pseude first order (PFM st) and Pseudo second order (PSM nd) for fluoride (F-) removal using two-bio adsorbents. It can be seen readily that pseudo second order (PFM nd) is the good model for (F-) adsorption because it gives better results for all adsorbents where the root mean square error (R2) was above 0.99. The rate constant and the amount of adsorbed of (F-) separation for all adsorbents were founded depending on the result in Fig. 3 which are presented in Table 2. In this study, the solid- liquid separation kinetics is observed by selecting the rate-limiting stage of a solute Fig. 4. Thus, both exterior mass transfer and internal diffusion were used to study the adsorption process. Internal particle diffusion takes place with high speed of agitation (120 rpm) during the experiment. First linear part of the plot illustrates the boundary film diffusion and second part of the linear portion illustrates intraparticle diffusion according to theory of diffusion (Gordon and Sweeny, 1980). The values of equation parameters (X max, Kd) for each adsorbent is given in Table 3.

\[ q_t = x_{max} + \left( K_d t^{1/2} \right) \]

Where: \( q_t \) is the capability of adsorption in (mg/g); \( x_{max} \) in (mg.g\(^{-1}\)), is the maximum capability in the intra particle diffusion and \( K_d \), constant rate in (mg. g\(^{-1}\).min\(^{-1/2}\)).

**Fig. 3a.** Pseude first model (PFM)st for different adsorbent. **Fig. 3b.** Pseude second model (PFM) nd plot for different adsorbent.
Table 1. Isothermal parameter results for the two adsorbents.

| Adsorbent          | Banana shell | Dehydrated orange juice remains |
|--------------------|--------------|---------------------------------|
| Temkin a           | 9.1100       | 17.8800                         |
| R2                 | 0.9760       | 0.8990                          |
| Temkin b           | 4210.5       | 12187.9                         |
| R2                 | 0.6900       | 0.9500                          |
| Langmuir max       | 1.3200       | 2.3400                          |
| R2                 | 0.9680       | 0.9880                          |

Table 2. Parameter results for the two kinetics models.

| Adsorbent          | Banana shell | dehydrated orange juice remains |
|--------------------|--------------|---------------------------------|
| Pseude first model (PFM) | q | 0.231 | 0.483 |
|                    | K₁          | 0.088 | 0.039 |
|                    | R²          | 0.966 | 0.975 |
| Pseude second model (PSM) | q | 0.791 | 1.38  |
|                    | K₂          | 0.295 | 0.434 |
|                    | R²          | 0.999 | 0.988 |

Table 3. Parameter results of intraparticle model diffusion.

| Adsorbent                      | Kd  | R²   | X max |
|--------------------------------|-----|------|-------|
| Banana shell                   | 0.027| 0.87 | 0.49  |
| Dehydrated orange juice remains| 0.033| 0.93 | 1.19  |

4.2. Reducing fluoride from artificial solution

4.2.1. Influence of zirconyl chloride absorption temperature

In this study, the loading quantity of Zirconyl chloride was optimized and investigated using four different types of Zirconyl chloride – dehydrated orange juice remains mixture prepared at different temperatures at 20, 30, 40 and 50 ºC because the development of dynamic adsorption sites for fluoride removal on dehydrated orange juice remains is dependent on. Table 4 displays the effect of Zirconium temperature on the quantity of Zirconium loaded. It is showed that the dehydrated orange juice remains (dejr) increased with increasing temperature of the loading reaction, thus, the loading of Zirconium on (dejr) at higher temperatures degree is more
advantage for fluoride (F) removal. Fig. 5 shows the breakthrough curves of four different types of Zirconyl chloride – dehydrated orange juice remains (Zc-dejr) for reducing (F) from drinking water. In the case of (Zc-dejr) prepared at above 303 K temperature, the performance of adsorption for fluoride removal appeared to be more preferable in comparison to lower (223 K) temperatures. The uptake capability (quc) of (Zc-dejr) prepared at 223, 293, 303, and 313 K for (F) were found to be 7.15, 11.30, 11.41 and 11.44 mg.g$^{-1}$, respectively. Table 4 showed that the treating volume is increased from 457 ml to 648 ml as the preparing temperature of (Zc-dejr) is increased from 293 K to 313 K which that recognized the increase in active adsorption sites for fluoride removal. The experiments operation parameters were fixed on 4 of alkalinity; 15.1 of influent concentration; 3.12 ml/min of flow rate, 3 cm of bed depth.

| Zirconyl chloride loading | Temperature (K) | Flow rate (ml/min) | $t_2$ (sec) | $t_1$(sec) | Bed height (cm) | q_{aps} | qt |
|--------------------------|-----------------|-------------------|------------|----------|----------------|--------|----|
| 66.3                     | 223             | 3.12              | 15.1       | 7500     | 1200           | 3      | 7.15 | 4.06 |
| 87.6                     | 293             | 3.12              | 15.1       | 9900     | 3300           | 3      | 11.30 | 6.11 |
| 87.9                     | 303             | 3.12              | 15.1       | 12000    | 4500           | 3      | 11.41 | 6.16 |
| 88.2                     | 313             | 3.12              | 5.40       | 12900    | 5100           | 3      | 11.44 | 6.19 |

4.2.2. Effect of inlet fluoride

This research investigate influence of inlet nickel concentration because it provides an significant driving force to incredulous the mass transfer resistance of component for both
phases, solid with liquid. Different concentration of fluoride solutions (15.1, 30, and 5 mg L⁻¹) was taken as the feed concentration to the absorber column. As the influent fluoride concentration increased to 30 mg/L, the adsorption process reached to the highest level more quickly and the breakthrough period was shortened (less than 4200 sec). Fig. 6a shows that fluoride removal (F⁻) rate was reduced with inlet concentration increasing because of the fixed dosage of adsorbent capability is flooded at 30 mg/l concentration. This result was the same as the result reported by Neem charcoal (Chen and Wu, 2004). The amount of fluoride uptake also increased from 5.5 to 7.3 ppm with influent fluoride (F⁻) increasing from 5 to 30 ppm. This result is agreed with (Baral, et al., 2009) that attributed that greater driving force (concentration difference) for the transfer zone is achieved at high concentration to generate the mass transfer resistance in the fixed absorption column.

4.2.3. Influence of influent alkalinity
The influence of alkalinity on fluoride removal rate and the breakthrough profile was studies in the range of pH (3.5-6.5) and results are illustrated in the Fig. 6e. It was observed readily that the breakthrough profile was increased by increasing pH from 3.5 to 4.5, and then decreased to 4.5 in the range of 4.5 to 6. This concludes that occurrence of the breakthrough was prolonged to 15000 sec with the greatest extent pH of 4.5, therefore suggesting that the optimum adsorption of fluoride is achieved at this value.

4.2.4. Influence of feed discharge
Influence of feed discharge solution on the adsorption behavior was studied with discharge rates of 0.91 and 2.55 ml/min while maintaining the same inlet fluoride of (15.1 mg/l), bed depth (4 cm), and pH of the feed solution (pH = 4.5) constant at room temperature. The breakthrough data presented in Fig. 2c indicates that the increasing flow rate led to decrease the breakthrough period because the low discharge rate increase the interaction period between the fluoride ions (F⁻) and the adsorbents of banana shell and orange shell surface. The adsorption capacity of fixed bed column was increased from 5.6 to 6.2 mg.g⁻¹ by decreasing the discharge rate from 0.05 to 0.02 ml. sec⁻¹ as shown in Fig. 6c.

4.2.5. Influence of bed depth and grain size
Fig. 6c illustrates the influence of bed height on breakthrough profile of fluoride with different bed height between (3-6). It can be observed from this figure, the breakthrough period and treated capacity of fluoride (F⁻) increases with increment the fixed bed height depth. The absorption capacity at 1.5, 3, 4, and 6 cm bed height were calculated as 14.09, 11.3, 7.88 and 5.77 mg.g⁻¹, respectively, Table 5 proposing that the channeling effect observed increased with
increasing height of the column, that reducing the column capacity. This influence may be reduced by increasing the diameter of the column. It was observed, when the grain size of the particle increases, the thickness of the stagnant film around the particles increases, and the total length of the path inside the pores increases. Under these conditions, the overall removal efficiency is slow. It was observed that the increasing of grain dimension of adsorbent decreases both the breakthrough time and the maximum bed capability. Thus, the performance of adsorption is better with small grain dimensions, but the small grain causes to raise the flow resistance of the column. Thus, this study was carried out with small grain size ranged between (0.5-1) mm and with optimum dose range of 6-20 gm/l.

![Fig. 6a. Breakthrough profile of fluoride removal at different initial fluoride concentration with (Zc-dej) adsorbent.](image)

![Fig. 6b. Breakthrough profile of fluoride removal at different flow rate.](image)

![Fig. 6c. Breakthrough profile of fluoride removal at different bed depth.](image)

![Fig. 6d. Breakthrough profile of fluoride removal at different alkalinity.](image)

### 4.3. Bed depth check time model (BDCTM)

The initial part of the breakthrough profile is selected by a simple mathematical model of fixed bed depth which expressed by the following equation:

\[
 t_f = \frac{A_p \cdot Z}{C_i \cdot v} - \left( \ln \left( \frac{C_r}{C_{br}} - 1 \right) * \frac{1}{K_G} \right)
\]

Where: \(C_{br}\) and \(C_r\), breakthrough and inlet fluoride concentration (mg.l-1); \(A_p\), adsorption potential; \(v\), the linear velocity (cm.min-1) in the fixed bed column; \(Z\) is the depth of the fixed bed.
bed (cm) and k is the kinetic constant (l. mg-1 min-1). Fig. 7 shows the linear relation between the breakthrough profile, and bed height. $A_p$ and $k$ were determined from the slope and intercept of the line in Fig. 7 as $9.1 \times 10^{2}$ mg/l and $6.1 \times 10^{-3}$ l/mg min, respectively. The high value of the check time model adsorption potential, $A_p$, for the present system with high correlation regression coefficient likely describes the high adsorption efficiency of the (Zc-dejr) adsorbent bed, certifying the validity of check time model for the proposed system.

![Fig. 7. Relationship between breakthrough check time with depth (MODEL RESULT).](image)

### 4.4. Comparative technical with other methods

Table 6 listed the comparison of adsorption removal efficiency for fluoride removal of several adsorbent in the bed absorption column with those of (Zc-dejr) and banana shell. It can be observed, the new adsorbents of (Zc-dejr) investigated in this research is illustrating its potential as a capable material for fluoride (F-) decreasing from drinking water whereas the removal rate was more than 92%. (Zc-dejr) was (93 %) which it was more effective for fluoride (F-) removal then banana shell and other methods. The adsorption mechanism to adsorpe t the pollutant (F-) on (Zc-dejr) and banana shell was found to be complex. The intra-particle diffusion besides external adsorption donates to rate –limiting stage. The proposed explanation for this observation, the significantly high adsorption capacity attributable to the increase of effective adsorption sites for fluoride on to polymer matrices of the (Zc-dejr) adsorbent loadings.

### 4.5. Treatment of actual waste plating using the new adsorbent of (Zc-dejr)

In this study, the new adsorbent of (Zc-dejr) was used using actual waste plating solution in the bed column for investigating the application of Zc-dejr in water treatment containing trace of fluoride (F-). Table 7 shows the characteristics of the waste plating mixture which where it was identified as containing several cationic. The operation condition for the elution process was 0.05 ml/sec of flow rate; 15.5 of inlet fluoride concentration; 1.5 cm of bed depth; 25 °C of temperature degree and the eluent process was implemented with 0.1 M of hydroxide sodium.
Table 5. Comparative study for fluoride removal using various adsorbents with optimum operation parameters (Karthikeyan, 2014)

| Adsorbents          | Q, mg/g | °C | Removal rate % | pH | References                  |
|---------------------|---------|----|----------------|----|-----------------------------|
| Laterite            | 0.34    | 20 | 66.9           | 4  | Deng et al. (2011)          |
| bio composite       | 1.7     | 5  | 70.1           | 4.5| Fang et. al (2003)          |
| Chitin              | 3.4     | 5  | 45.9           | 4.8| Fang et. al (2003)          |
| Acid treated GHB    | 0.16    | 2.8| 51%            | 7.2| Singh et al. (2012)         |
| Granular red mud    | 0.78    | 20 | 69.8           | 4.7| Singh et al. (2003)         |
| Kanuma mud          | 1.22    | 20 | 61.3           | 6.9| Tor et.al (2009)            |
| Saw dust raw        | 0.89    | 5  | 49.7           | 6  | K.Y.Ashishet.al             |
| Neem papal          | 1.6     | 5  | 85.3           | 2  | K.Y.Ashishet.al             |
| Available activated carbon | 1.3 | 5 | 57.6           | 6  | K.Y.Ashishet.al             |
| bone char           | 1.5     | 5  | 92             | 6  | Sabrina S. et al. (2011)    |
| Banana shell        | 0.79    | 15.1| 89.9           | 6.5| this research               |
| ( Zc-dejr)          | 1.38    | 15.1| 93.8           | 4.5| this research               |

Table 6. Characteristics of the waste plating mixture

| Component             | Concentration (mg/l) |
|-----------------------|----------------------|
| Almoium (Al+3)        | 12.6                 |
| Silica (Si+4)         | 37.1                 |
| Iron (Fe+3)           | 22.1                 |
| Calcium (Ca+2)        | 29.1                 |
| Copper (Cu+2)         | 8.30                 |
| Zinc (Zn+2)           | 0.85                 |
| Fluoride (F-)         | 15.5                 |
| Sulfuric acid (SO_{2^-}) | 525             |

The loaded fluoride (F-) was pulled out reactive the column for repeating the operation. The process was carried out in the batch system (Yue, et al., 2011) by 0.1 M of hydroxide to desorb the adsorbed fluoride from the filled column. Fig. 8, shows the elution profiles where the result showed that the fluoride quantity in the eluent was raised suddenly to 260 ppm after a discharge of 20 ML of 0.1 M hydroxide sodium composition which is greater than (15.1 mg/l) of the feed concentration by 17.8 times. The amount of adsorbed fluoride from the real waste plating solution onto the Zc-dejr was (1.65 mg/g) which is closely to the eluted quantity (1.61 mg/g).
5. CONCLUSION

Two adsorbents, banana shell and new adsorbents (Zc-dejr) were studied for decreasing fluoride (F-) in drinking water of Basra city. The results demonstrates the effectiveness of the new adsorbent, Zirconyl chloride – dehydrated orange juice remains (Zc-dejr) and banana shell for removal (F) from drinking water using fixed bed column where the removal efficiency was 94.4 and 89.8, respectively. Two models were used for the adsorption characteristics Temkin order (TIM) and Langmuir model. Langmuir model could successfully coincided the experimental data with the coefficient of determination (R2) of 0.95. It was concluded that the maximum adsorption capability for dehydrated orange juice remains adsorbent (Zc-dejr) is greater then Banana shell adsorbent. Both models of (PFM st) and (PSM nd) were used to study the adsorption kinetics of adsorption fluoride on bio adsorbents. It was concluded that PSM nd is give best result for (F-) adsorption. The adsorption capacity of fluoride (F) through a fixed column was dependent on solution alkalinity, depth of bed, inlet fluoride concentration, and discharge rate. It was increased with increment the adsorbent dose and decreasing size of the adsorbent. Optimum operating parameters that optimized in this research was 15.1 mg/l of feed concentration, 4 cm of bed depth and 4.5 pH of the feed solution. Effectiveness of continuous operations was evidenced by the effective removal of fluoride from actual waste plating solutions.

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