Fluoride Ions Removal using Yttrium Alginate Biocomposite from an Aqueous Solution

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\textbf{A B S T R A C T}

Removal of fluoride ions was investigated using a new adsorbent of yttrium alginate biocomposite (YALG). Effect of various parameters such as pH, contact time, initial concentration of fluoride ions and temperature on the sorption capacity of adsorbent was studied. Performing a mathematical assessment of fluoride sorption, isotherm and kinetics models including Freundlich & Langmuir isotherms and pseudo first & second order kinetics were applied on experimental equilibrium results through this work. Isotherm analysis revealed that Langmuir model showed a better evaluation from sorption equilibrium data than Freundlich. Based on kinetics evaluation, the pseudo second-order equation was capable of fitting the sorption data satisfactorily compared to the pseudo first-order model. The maximum sorption capacity of fluoride ions (q\textsubscript{m}, mg g\textsuperscript{-1}) using the YALG was found to be 147.05 mg g\textsuperscript{-1}. Regarding the thermodynamic studies and its parameters (i.e. $\Delta H$°, $\Delta S$° and $\Delta G$°) it is revealed that the fluoride ions adsorption using nanoporous YALG was feasible, spontaneous and endothermic in nature.

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\textbf{1. INTRODUCTION}

Biomaterials applications and usages have been extensively intensified in scientific areas such as biomedical, textile, chemical, environmental, etc. Recent researches on the environment, especially on the removal of hazardous materials, have led scholars paying much attention to natural materials as compared to the synthesized ones. Generally, due to their biocompatibility, natural abundance, fairly low cost, low toxicity, biodegradability, and sustainability features, these materials were considered over other synthesized components for practical purposes.

Alginate, regarded as an anionic biopolymer, is commercially extracted from brown algae including \textit{Laminaria hyperborea}, \textit{Laminaria digitata}, \textit{Laminaria japonica}, \textit{Ascophyllum nodosum}, and \textit{Macrocystis
pyrifera [1]. Resemblance of alginate structure to an extraordinary matrix with so many hollows converts it to a pertinent medium for holding metal elements, which can be used in the realm of removal of harmful materials in environmental protection fields. This linear copolymer comprises of blocks of (1,4)-linked β-D-mannurionate (M) and α-L-gulurionate (G) residues, which has a lot of oxygen-containing and carboxyl functional groups on its surface. Such configuration allows them to exist in more than 200 different alginites type. These materials have found great importance for the heavy metal adsorption [2-4]. Besides, functionalization of alginate compounds converts them to precious materials for synthesizing novel sorbents for utilizing in the removal of hazardous materials. Functionalizing with chitosan [5], cyanex 272® [6, 7] or bentonite [8] to intensify alginate capability for the uptake of Cu(II), Co(II), and Cd(II) are just a few instances.

It is well known that fluoride, a hazardous anion, has several toxicological impacts on human health. Considering trivial amount of fluoride ions beneficial for both human and animal, long-term ingestion of fluoride as in potable water causes severe chronic toxicity especially to skeletal structure. Mottling of teeth and softening of bones, ossification of tendons and ligaments are only a few symptoms of excess exposure to fluoride ions [9]. High-tech industries including semiconductor and integrated circuits manufacture and effluents of manufacturing glass industries propagate a large amount of fluorine into the environment [10, 11]. The World Health Organization has set a maximum value of 1.5 mg/L for fluorine in potable water [11]. Among traditional routes for removal of fluoride, precipitation using flocculation/coagulation techniques with calcium/magnesium compounds has been intensively investigated [12-14]. However, it is understood that this method has low capability for efficiently uptaking fluoride from the polluted water bodies. Thus, it has been felt that there is a demand for new processes for complete removal of such hazardous material from environments.

Removal of fluoride ions has been investigated by many researchers in recent decade. Kaygusuz et al. [15] investigated the fluoride removal using aluminum alginate. They found that maximum sorption capacity for fluoride ions was 75.2 mg g⁻¹. In 2015, another research was carried out for the synthesis of alginate beads filled with nanohydroxyapatite for the sake of fluoride ions uptake [16]. In this work defluoridation was successfully done by the hibridized alginate biopolymers and governed by adsorption, complexation, and ion exchange. Swain et al. [17] prepared a new composite material containing biopolymer alginate beads with mixed metal oxides. The measured monolayer sorption capacity for this work was reported as qₘₐₓ=1.438 mg g⁻¹ based on the Langmuir bonding model.

Removal of fluoride ions from aqueous solution using a new adsorbent based on alginate is subject of the current study. First part of the present work was dedicated to the preparation of adsorbent and its ability for fluoride removal. These experiments were carried out for investigation of the impact of parameters such as pH, initial concentration of fluoride, contact time and temperature on the sorbent performance. Explanation of the process using mathematical models: isotherm, kinetics and thermodynamics, formed the final part of the present study.

2. EXPERIMENTAL

2. 1. Materials

A stock aqueous solution of sodium fluoride, NaF, used in the sorption tests was prepared by dissolving a certain amount of NaF with 99.99% assay in distilled water. Sodium alginate was obtained from Sigma-Aldrich (Milwaukee, WI, USA). YCl₃ and all other reagents employed in present work were analytical grade from Merck (Darmstadt, Germany).

2. 2. Yttrium Alginate (YALG) Preparation

Yttrium alginate beads were prepared as previously described by Yakuan et al. [18]. 0.2 mol·l⁻¹ YCl₃ solution and 2% (w/v) sodium alginate solution were prepared and mixed using a mechanical stirrer. The sodium alginate solution was added into the YCl₃ solution using a 0.3 mm medical needle. Gel type spherical beads were formed during this process. For hardening the formed beads, it was gently stirred in the above mentioned solution for 3 h. The prepared beads were washed three times with pure water and, finally, dried at 40 °C for about 10 h.

2. 3. Fluoride ions Sorption Experiments

Adsorption tests were carried out to evaluate the YALG adsorbent efficacy for fluoride ions removal from aqueous solution. In these tests, 20 mg of the YALG adsorbent were introduced into 10 ml of sodium fluoride solution with a certain initial concentration. Resulted solution was agitated for an appropriate time so that equilibrium was attained. Then adsorbent was filtered from the solution and fluoride ions concentration of the remained solution was measured using a fluoride ion-selective electrode (F-ISE).

Once Cᵢ and Cₑ for fluoride content was determined, the adsorption capacity (q, mg g⁻¹) and adsorption percentage (uptake, %) were calculated using the following equations (Equations (1) and (2)) :

\[ q(\text{mg g}^{-1}) = (Cᵢ - Cₑ) \times \frac{V}{m} \]  

(1)
Uptake% = \( \left( \frac{C_0 - C_1}{C_0} \right) \times 100 \) (2)

2. 4. Working Solution pH Effect In order to assess the effect of working solution pH on the adsorption behavior of the YALG adsorbent, the adsorption experiment was conducted at varied pH values in the range of 2-9. In a typical procedure, 20 mg of the YALG at various pH values was introduced into 10 ml of the fluoride solution whose initial concentration was situated on 50 mg.l\(^{-1}\) of fluoride ions.

2. 5. Isotherm Analysis In order to perceive better understanding of the relationship between the amount of fluoride ions adsorbed on the YALG surface and concentration of extant metal ions in solution, isotherm modeling was carried out. Binding models including the Freundlich and Langmuir equations, which are widely used to understand the sorption mechanism, were utilized to describe the experimental result of sorption isotherm. The Freundlich and Langmuir equations are mathematically expressed as (Equations (3) and (4)):

Langmuir isotherm:
\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} k_l
\]

Freundlich isotherm:
\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]

2. 6. Kinetics Modeling To demonstrate the effect of contact time on the fluoride sorption process using the YALG sorbent, kinetic studies were performed with C\(_0\)(F)= 50 mg.l\(^{-1}\), m\(_{\text{YALG}}\)=0.02 g, and pH=5.5. On that sake, kinetic models were applied on equilibrium data to discover the rate-limiting step of sorption process such as chemical reaction or mass transfer. Kinetics models including pseudo first-order and second-order were used for fluoride sorption onto YALG sorbent. The pseudo first-order and second-order are respectively formulated as (Equations (5) and (6)) [19]:

Pseudo first-order model:
\[
\log \left( \frac{q_e}{q_{\text{max}} - q_e} \right) = \left( \frac{K_l}{2.303} \right) t
\]

Pseudo second-order model:
\[
\frac{t}{q_t} = \frac{1}{K_q q_{\text{max}}} + \frac{t}{q_{\text{max}}}
\]

2. 7. Temperature Effect The temperature effect on the fluoride sorption was investigated at C\(_0\)(F)= 50 mg L\(^{-1}\), m\(_{\text{YALG}}\)=0.02 g, pH=5.5, and the fluoride uptake as a function of temperature was sketched. Thermodynamic study was conducted in order to reveal the nature of the sorption process. Thermodynamic parameters for fluoride adsorption onto YALG were determined using the following equations (Equations (7)-(9)):

\[
K_d = \left( \frac{C_e - C_1}{C_1} \right) \frac{V}{m}
\]

\[
\ln K_d = \frac{\Delta H^\circ}{R} - \frac{\Delta S^\circ}{RT}
\]

\[
\Delta G^\circ = -RT \ln K_d
\]

3. Results and Discussion

3. 1. pH Effect Figure 1 shows the plot of fluoride sorption capacity of YALG adsorbent versus pH. At acidic medium, the results showed that the sorption capacity of the adsorbent was higher than alkaline situation. Metal ion Y attached to the sodium alginate and completed their coordination shell with -COOH group, meanwhile, Y can bond with Cl\(^-\) or OH\(^-\). In the acidic pH, Cl\(^-\) first exchanged with F\(^-\) due to the advantage in activity, which was a replacement reaction. Then, OH\(^-\) exchanged with F\(^-\). These OH\(^-\) ions can bind or release protons depending on the initial solution pH. Under acidic conditions, more OH\(^-\) existed, enhancing the adsorptin capacity for fluoride. This is confirmed by increasing the adsorption capacity with decreasing pH. The maximum fluoride adsorption capacity is at pH 4-5, as shown in Figure 1. With more acidic pH, a significant decline in fluoride sorption capacity is observed, which may be due to the formation of hydrofluoric acid. With alkaline pH, a significant decline in fluoride sorption capacity is observed, which may be due to the higher concentration of OH\(^-\) ions. We propose the following reaction mechanism for the adsorption of fluoride ions by YALG:

ALG-YCl + F\(^-\) \rightarrow ALG-YF + Cl\(^-\) (10)

Or ALG-YOH + F\(^-\) \rightarrow ALG-YF + OH\(^-\) (11)

ALG-YOH\(^+\) + F\(^-\) \rightarrow ALG-YF + H\(_2\)O (12)

The overall mechanism can be written as:

ALG-YOH + H\(^+\) + F\(^-\) \rightarrow ALG-YF + H\(_2\)O (13)

With neutral pH reaction, reaction (10) occurs prior to (13). Cl\(^-\), initially attached to yttrium alginate, is replaced by F\(^-\). With acidic pH, reaction (13) is more prevalent through exchange mechanism [20].

3. 2. Isotherm Study The adsorption capacity as a function of initial concentration of fluoride ions were investigated in the range of 0 to 350 mg.l\(^{-1}\) at the pH of 5.5 with 20 mg of YALG adsorbent. The sorption of fluoride ions increased with the increase in the initial concentration of fluoride ions (See Figure 2a). To
determine which model more accurately describes the adsorption process at different initial concentrations, plotting of Freundlich and Langmuir isotherm models was carried out in Figures 2b and 2c, respectively, and they were compared with each other regarding their correlation coefficient \( R^2 \). The values of isotherm model constants were also calculated and reported in Table 1.

As seen, the sorption results of fluoride ions onto YALG are in good agreement with the Langmuir model compared to Freundlich model. Thus, description of fluoride sorption process using YALG sorbent can be ascribed to the monolayer uniform adsorption and a homogeneous surface with identical binding sites. The maximum sorption capacity reached 147.05 mg g\(^{-1}\) at pH 5.5. Our results is in close agreement with that reported in the literature [18].

### 3.3. Kinetics Studies

Removal of fluoride ions using YALG sorbent as a function of contact time ranging from 0 to 25 h was plotted in Figure 3a. From the Figure, it is clear that 2 h was adequate for attaining the sorption equilibrium. Determining the rate of metal sorption as an important factor defining the sorption effectiveness, experimental data were fitted by pseudo first-order and second-order kinetics as shown in Figures 3b and 3c, respectively. The kinetics parameters and correlation coefficient \( R^2 \) are listed in Table 2. Considering \( R^2 \) values, the pseudo second-order model provided better mathematical description of sorption experimental data of the adsorbent YALG than that of the pseudo first-order. The conformity of pseudo second-order model discloses that the concentration of both sorbent (YALG) and sorbate (fluoride ions) are involved in the rate-limiting step of the sorption process [21].

### 3.3. Temperature Effect

Thermodynamic evaluation of fluoride sorption onto YALG was studied once the effect of temperature on sorption performance of the sorbent was revealed. To do so, the value of Ln\( K_d \) was plotted versus \( 1/T \) as depicted in Figure 4. As shown in this Figure, increasing the temperature obviously led to the increase in \( K_d \) value, indicating that the sorption of fluoride ions onto YALG is an endothermic process.

According to Equations (7)-(9), Table 3 shows the thermodynamic parameters including \( \Delta S^o \), \( \Delta G^o \), \( \Delta H^o \) and corresponding correlation coefficients. Sorption feasibility is indicated from the positive quantity of \( \Delta S^o \). Noticeably, the \( \Delta G^o \) values descend with ascending temperature, denoting higher spontaneity at higher temperatures.

### Table 1. Isotherm constants for fluoride ions uptake onto YALG sorbent

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_{max} ) (mg g(^{-1}))</td>
<td>147.05</td>
</tr>
<tr>
<td></td>
<td>( K_l ) (mg g(^{-1}) M(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>( n )</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>( k_f ) (mg g(^{-1}) mM(^{-1}))</td>
<td></td>
</tr>
</tbody>
</table>
To demonstrate the synthesizing procedure for a Cu mic-

TABLE 2. Kinetic parameters for fluoride removal using YALG sorbent

<table>
<thead>
<tr>
<th></th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( q_e ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first-order</td>
<td>0.072</td>
<td>3.66</td>
<td>0.275</td>
</tr>
<tr>
<td>Pseudo second-order</td>
<td>0.41</td>
<td>54.64</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Figure 3. (a) Effect of time on fluoride sorption performance of YALG adsorbent, (b) adsorption kinetics curve of pseudo first-order model and (c) linearized experimental data of pseudo second-order kinetic model

TABLE 3. Thermodynamic parameters of fluoride ions removal using YALG at different temperatures

<table>
<thead>
<tr>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.835</td>
<td>0.0805</td>
<td>-17.16</td>
<td>-18.77</td>
</tr>
<tr>
<td>318</td>
<td>338</td>
<td>0.8485</td>
<td>20.3</td>
</tr>
</tbody>
</table>

It the Gibbs free energy change for physisorption is generally between -20 and 0 kJ mol\(^{-1}\), for physisorption along with chemisorption is within -20 to -80 kJ mol\(^{-1}\), and for chemisorption is in the range of -80 to -400 kJ mol\(^{-1}\) [21]. The amount of \( \Delta G^\circ \) suggests the physisorption nature of fluoride ions removal using YALG sorbent.

4. CONCLUSION

Here, we demonstrate the synthesizing procedure for a biocomposite sorbent comprising alginate and yttrium and its sorption characteristics for the removal of fluoride ions. Using mathematical models including isotherm binding and kinetic equations, we provided an explanation of the fluoride sorption onto YALG adsorbent. According to isotherm analysis, the Langmuir model fitted the experimental data better than the Freundlich model demonstrating homogenous surfaces with identical binding sites for YALG. As the kinetic studies revealed, fluoride ions sorption equilibrium data can be satisfactorily represented by the pseudo second-order model indicating that the concentration of both sorbent and sorbate control the rate-limiting step of the sorption process. The calculated Gibbs free energy changes suggest that the sorption process of fluoride ions onto YALG could be considered as physisorption process. Sorption feasibility, spontaneous and endothermic nature of the adsorption was also revealed by the thermodynamic studies, regarding \( \Delta S^\circ \) and \( \Delta H^\circ \) values.

5. REFERENCES

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\textbf{RESEARCH NOTE}

\textbf{چکیده}

هدف این پژوهش بررسی جذب یون فلورید با استفاده از جذب جدیدی برای کامپوزیتی (YALG) برای کمک به کاهش میزان یون فلورید در محیط‌های آبی مطرح می‌باشد.

پارامترهای مختلف به منظور ارزیابی رابطه بازیابی یون فلورید، مدل‌های سیستمی و ایزوترم فیزیکی و شیمیایی مورد بررسی قرار گرفت. مدل‌های جذب YALG با داده‌های تعادلی در شرایط متنوع تحقیقات عملیاتی شاد با وجود مقدار مختلف میزان یون فلورید، مدل‌های سیستمی و ایزوترم فیزیکی شامل مدل فروندلیچ و لانگمویر و مدل‌های سیستمی شامل مدل فروندلیچ و لانگمویر و M. Kosari and H. Sepehrian / IJE TRANSACTIONS A: Basics Vol. 30, No. 1, [January 2017] 1-6


\textbf{NOTE}