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This investigation provides new insights into the effective removal of tetrafluoroborate (BF_4^-) by means of bio-sorption on waste generated in the orange juice industry. It was undertaken to evaluate the feasibility of zirconium(IV)-loaded saponified orange waste gel for BF_4^- removal from an aqueous solution. Batch adsorption experiments were carried out to study the influence of various factors such as pH, presence of competing anions, contact time, initial BF_4^- concentration and temperature on the adsorption of BF_4^-. The optimum BF_4^- removal was observed in the equilibrium pH region 2–3. The presence of co-existing anions showed no adverse effect on BF_4^- removal except SO_4^{2-}. The equilibrium data at different temperatures were reasonably interpreted by the Langmuir adsorption isotherm and the maximum adsorption capacities were evaluated as 2.65, 3.28, 3.87 and 4.77 mmol g^{-1} at 293, 298, 303 and 313 K, respectively. Thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated that the nature of BF_4^- adsorption is spontaneous and endothermic. The results obtained from this study demonstrate the potential usability of orange waste after juicing as a good BF_4^- selective adsorbent.

Keywords: adsorption; kinetics; orange waste; zirconium(IV) loaded adsorbent; thermodynamics

1. Introduction

The disposal of polluted water into the environment is a major problem in industrialized countries [1]. The removal and recovery of hazardous ions from industrial effluents is a field of research receiving increasing attention from the practical point of view in scientific community. Tetrafluoroborate (BF_4^-) is formed by the combination of fluoride, a highly electronegative element, with boron in the form of boric acid under certain conditions. The wastewater from plating plants as well as from coal-fired boilers, which contain boron and fluorine, disposes a considerable amount of BF_4^- into the environment.

In order to overcome such pollution from industrial wastewater, attempts at adsorptive removal of BF_4^- has been carried out using a low-cost adsorbent. Conventionally, fluoride has been removed by adding $Ca(OH)_2$ to form CaF_2, which is sparingly soluble in water. However, with this conventional method, the concentration of fluoride cannot be lowered below 5 mg dm^{-3}, theoretically, or 15 mg dm^{-3}, in practice, while the acceptable limit for discharge into the environment is only 0.8 mg dm^{-3} in Japan [2]. However, the fluoride in the form of BF_4^- cannot be removed by this method because the $Ca(BF_4^-)_2$ formed after the combination of calcium and BF_4^- ions is water soluble. After decomposition of BF_4^- by interaction with aluminium under acidic conditions, according to the reaction shown below, fluoride and boron are individually removed by means of conventional methods [3].

$$\begin{aligned} &2Al_2(SO_4)_3 + 3HBF_4 + 9\ H_2O \\ &\quad = 4\ AlF_3 + 6\ H_2SO_4 + 3\ H_3BO_3 \end{aligned}$$

However, this method is tedious and can become expensive. Consequently, there is the urgent need to develop technology for the direct removal of BF_4^- from aqueous solution [4]. However, very little work has been reported to date in the literature for the direct removal of BF_4^- from aqueous solution. Yoshioka *et al.* studied the removal of BF_4^- from an aqueous solution by using magnesium–aluminium oxide (Mg–Al oxide) produced by thermal decomposition of a hydrotalcite-like compound. They found that the reduction in the concentration of BF_4^- is achieved only by the uptake of Mg–Al oxide and not by the hydrolysis of BF_4^- [5].

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Removal of hazardous ions from wastewater can be achieved by several techniques, such as chemical precipitation [6], adsorption processes or an ion exchange method [7], co-precipitation, an evaporation–crystallization process and solvent extraction processes [8]. All these technique typically require considerable capital investment and operating costs for infrastructure and reagents. Much attention has been paid to bio-sorption as a novel technology for the removal of pollutant ions from aqueous solution, taking account of the high binding capacities of various biological wastes. The main advantages of bio-sorption over conventional methods are low cost, high efficiency, minimization of the production of a toxic chemical and biological sludge, and the possibility of recovery and regeneration of the bio-sorbent [9].

The use of waste biomass after some modification is considered a promising technology for the removal of BF_4^- from aqueous solution. Biomass wastes like orange waste, with a large amount of surface functional group, may be good alternatives to expensive synthetic adsorbents. In our previous papers, Zr(IV) loaded orange gel was utilized for the effective removal of arsenic and phosphate from an aqueous medium [10,11]. In this paper, modified orange waste after zirconium loading was employed for the effective removal of BF_4^- ion from aqueous solution.

2. Experimental

2.1. Chemicals and analysis

All chemicals used were of analytical grade and used without further purification. Tetrafluoroborate stock solution ($1000\,mg\,dm^{-3}$) was prepared by dissolving 1.26 g of sodium tetrafluoroborate (Wako Chemicals, Japan) in $1000\,cm^3$ of de-ionized water. The working solutions were prepared by diluting the stock solution. The pH of the BF_4^- solution was adjusted with the help of 0.5 M (M = mol dm^{-3}) HNO_3 and 0.5 M NaOH solution using a DKK-TOA model HM-25 G pH meter. The concentrations of the BF_4^- solution before and after adsorption were measured using Dionex model ICS; 1500 ion chromatography.

2.2. Preparation of Zr(IV)-loaded saponified orange juice residue

The preparation of the orange waste gel and the method of zirconium loading were described in detail in our previous paper [12] and as depicted by Scheme 1. The orange waste after juicing was kindly supplied by JA Saga Beverage Co., Ltd., Japan.

For the pretreatment, 100 g of orange waste was washed with distilled water to remove the water-soluble organic compounds that interfere with the saponification process. The pretreated orange waste was then mixed with 8 g of calcium hydroxide and crushed into fine particles with the help of a HITACHI VA-10 juice mixer. (This is for the saponification reaction where the methyl ester part of pectin in the orange waste is hydrolysed and pectin is converted into pectic acid.) The reaction mixture was shaken for 24 h at 303 K after the addition of a substantial amount of water to enhance the saponification reaction. The initial pH of the reaction mixture was adjusted to around 12 by adding some pellets of sodium hydroxide. After saponification, the suspension mixture was washed with distilled water followed by decantation and filtration until a neutral pH was achieved and finally dried in a convection oven at 343 K overnight.

The white product obtained in this way is a calcium-containing cation exchange gel, which is termed ‘saponified orange juice residue’ (SOJR). Thus prepared SOJR was further loaded with zirconium(IV) ion as follows. Three grams of SOJR were placed in a conical flask along with $500\,cm^3$ of 0.1 M zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) solution maintained at pH 2.11. The mixture was then agitated for 24 h at 303 K for complete zirconium loading. After filtration, it was washed several times with distilled water followed by a hot water wash to remove free zirconium(IV) ion from the gel. It was dried in a convection oven at 343 K overnight. The product was ground in a mortar and sieved to obtain the particle size of 100–150 μm gel.

An adsorbent prepared in this way is termed a zirconium-loaded saponified orange juice residue (Zr-SOJR). The zirconium content in SOJR was investigated by totally dissolving 50 mg of Zr-SOJR in $10\,cm^3$ of aqua regia. After filtration, the zirconium concentration in the filtrate was measured using a Shimadzu model ICP/AES-8100 spectrometer and evaluated as $1.62\,mmol\,g^{-1}$ of dry SOJR.

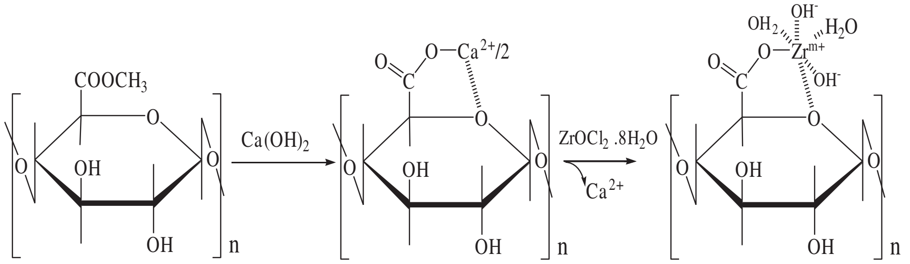
The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR).

2.3. Batch wise adsorption tests

The adsorption behaviours of Zr-SOJR for BF_4^- were examined under a batch mode of operation. In the batch wise adsorption studies, 10 mg of Zr-SOJR was shaken together with $10\,cm^3$ of BF_4^- working solution in a $50\,cm^3$ conical flask in a thermostated air bath incubator (THOMAS thermostated shaking incubator AT24R) at a rotating speed of 150 rpm for 24 h, after which the suspended mixture was filtered and residual concentrations in the filtrate were measured. The effect of pH on BF_4^- adsorption was examined at different pH values between 1 and 8 at $50\,mg\,dm^{-3}$ BF_4^- concentration. Adsorption isotherms were measured in varying BF_4^- concentrations ($50–1000\,mg\,dm^{-3}$) at different temperatures (293, 298, 303 and 313 K) at constant pH (pH = 2). The percentage adsorption (% A) and the adsorption amount of BF_4^- on the adsorbent (q, $mmol\,g^{-1}$) were calculated according to Equations (1) and (2),

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q = \frac{C_i - C_e}{W} \times V \quad (2)$$



Scheme 1. Synthetic route for Zr-SOJR.

where C_i and C_e (mmol dm^{-3}) are the BF_4^- concentrations before and after the adsorption, respectively, V (cm^3) is the volume of the test solution and W (mg) is the dry weight of the adsorbent.

All experiments were carried out in duplicate and the average results were recorded.

2.4. *Kinetic studies*

For the kinetic studies, 20 mg of Zr-SOJR was placed in a 50 cm^3 conical flask together with 10 cm^3 of the BF_4^- working solution (50 mg dm^{-3}) at pH 2. The flasks were shaken at different temperatures (293, 298, 303 and 313 K) at a speed of 150 rpm. Samples were collected at predetermined time intervals (13 different times). The samples were filtered immediately through filter paper and the filtrate was analysed to determine that the concentration of BF_4^- remains in the filtrate.

3. Results and discussion

3.1. *FTIR analysis*

The FTIR spectra of Zr-SOJR before and after the adsorption of BF_4^- are shown in Figure 1. The band present at 3400 cm^{-1} is the stretching vibration of hydroxyl groups (−OH) and that at 1636 cm^{-1} is due to the stretching vibration of the carbonyl (−C=O) group of pectic acid [13]. The peak around 1636 cm^{-1} is shifted to the lower frequency region, which may be to due the adsorption of BF_4^- on Zr-SOJR (Figure 1b). Because, hydroxyl ions are replaced by BF_4^- during the adsorption of BF_4^- (as described in detail later), the shift to low frequency is due to the replacement by the high molecular weight of the exchange anion [14].

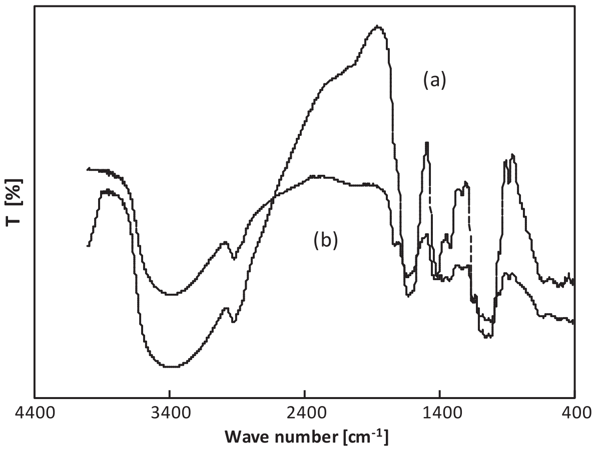


Figure 1. FTIR spectra of Zr-SOJR before and after the adsorption of BF_4^- (a) before adsorption and (b) after adsorption.

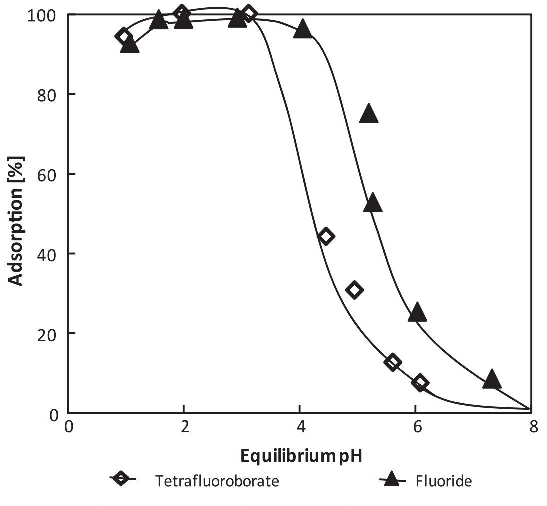
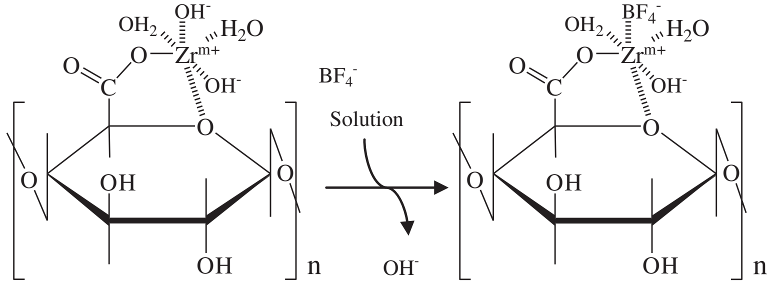


Figure 2. Effect of pH on the adsorption of BF_4^- and F^- onto Zr-SOJR. Conditions: concentration of BF_4^- in feed solution = 50 mg dm^{-3}; concentration of F^- = 10 mg dm^{-3}; dry weight of Zr-SOJR added = 10 mg; volume of test solution = 10 cm^3; shaking time = 24 h; temperature = 303 K.

3.2. *Influence of pH for the adsorption of BF_4^-*

The pH of the solution has been identified as the most important variable governing adsorption [15]. Figure 2 shows the influence of equilibrium pH on the adsorption of BF_4^- on Zr-SOJR together with that of fluoride for comparison. The result shows that the optimum adsorption of BF_4^- on Zr-SOJR took place in the pH region between 2 and 3. The percentage adsorption gradually increases with increasing pH (between 0.97 and 2) and then tends to approach a maximum value (100%) up to pH 3, after which it decreases sharply with a further increase in pH. It is seen from Figure 2 that the Zr-SOJR exhibits similar behaviour for the adsorption of fluoride.



Scheme 2. Ligand exchange mechanism of BF_4^- adsorption onto Zr (IV)-SOJR.

In both cases, the decrease in adsorption at pH greater than 3 (BF_4^-) and at pH greater than 4 (F^-) is due to the competition with hydroxyl ion for the fixed number of adsorption sites. The results of the adsorption experiments can be interpreted by a ligand exchange mechanism between the anionic species (BF_4^- and F^-) and hydroxyl ions coordinated on the zirconium ion immobilized on the SOJR as shown in Scheme 2. This result is consistent with the fluoride adsorption on Zr(IV)-impregnated collagen fibre [16] and also with the adsorption on La(III)-impregnated cross-linked gelatin [17].

3.3. *Adsorption kinetics*

Figure 3 shows the time variation in the amount of the adsorption of BF_4^- on Zr-SOJR at pH 2 at different temperatures. It is clear that the temperature effect on the adsorption rate is insignificant below 303 K but that it is significantly enhanced at 313 K. That is, it is apparent from Figure 3 that the adsorption of BF_4^- increases slowly up to about 22 h and then subsequently tends to approach constant values in the cases of 293, 298 and 303 K. However, it increased rapidly up to 4 h and reached a constant value in the case of 313 K. Therefore, 24 h was considered necessary to achieve the complete adsorption of BF_4^- on Zr-SOJR in the subsequent adsorption experiments.

3.4. *Adsorption isotherms*

Figure 4 shows the adsorption isotherms of BF_4^- on Zr-SOJR at different temperatures. This figure indicates that the adsorption increases with rising temperature and increasing equilibrium concentration of BF_4^-. The adsorption increases at a low concentration of BF_4^-, whereas it seems to level off at high BF_4^- concentrations. This suggests the monolayer adsorption as described by the Langmuir model. The decrease in adsorption capacity with decreasing temperature indicates that the adsorption reaction of BF_4^- on Zr-SOJR is endothermic in nature. The data was further analysed by the Langmuir isotherm model as described in Equation (3),

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{3}$$

where q_e (mmol g^{-1}) represents the equilibrium amount of adsorption, C_e (mmol dm^{-3}) denotes the equilibrium concentration of BF_4^-, $q_{\max}$ (mmol g^{-1}) represents the maximum adsorption capacity, b (dm^3 mmol^{-1}) is the Langmuir

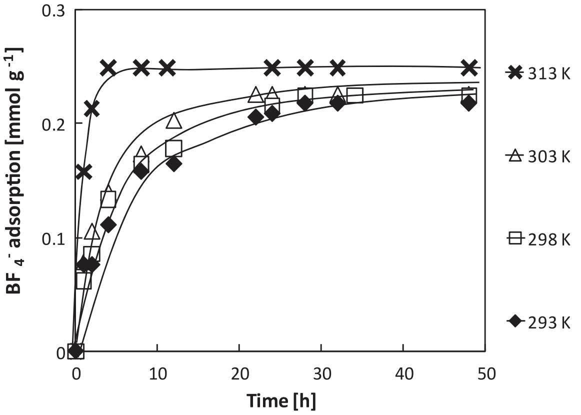


Figure 3. Adsorption of BF_4^- as a function of shaking time. Conditions: dry weight of Zr-SOJR added = 20 mg; volume of test solution = 10 cm^3; concentration of BF_4^- = 50 mg dm^{-3}; pH = 2.02.

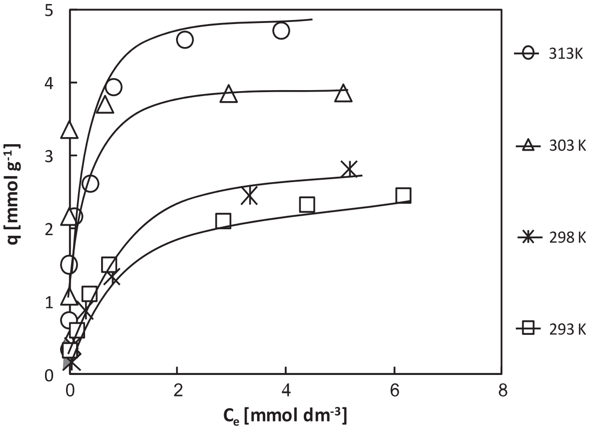


Figure 4. Adsorption isotherms of BF_4^- at different temperatures. Conditions: volume of test solution = 10 cm^3; dry weight of Zr-SOJR added = 10 mg; pH of solution = 2; shaking time = 24 h.

Table 1. Thermodynamic parameters calculated from the Langmuir constant b ($dm^3\ mmol^{-1}$) for the adsorption of BF_4^- onto Zr-SOJR.

Temperature [K]	q_{max} [mmol g^{-1}]	b [$dm^3\ mol^{-1} \times 10^3$]	$\Delta G^\circ = -RT \ln b$ [kJ mol^{-1}]	ln b	R^2
293	2.65	1.66	−18.06	7.41	0.99
298	3.28	1.85	−18.64	7.52	0.99
303	3.87	3.10	−20.77	8.24	1
313	4.77	10.51	−24.10	9.26	0.99

constant or equilibrium constant or binding constant related to the adsorption energy.

These adsorption isotherms demonstrate that Zr-SOJR may be used as an effective adsorbent for the BF_4^- removal from aqueous industrial effluents because of its high uptake capacity.

From the equilibrium constant, b ($dm^3\ mmol^{-1}$), derived from the Langmuir isotherm model at different temperatures, the thermodynamic parameters such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated with the adsorption process were calculated according to the following equations:

$$\Delta G^\circ = -RT \ln b \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

Thus,

$$\ln b = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

where R is the universal gas constant (8.31 J $mol^{-1}K^{-1}$) and T is the absolute temperature (K).

The plot of ln b against $1/T$ according to Equation (6) yields a straight line from which the enthalpy change (ΔH°) and the entropy change (ΔS°) were calculated from the slope and intercept, respectively. The change in Gibbs free energy (ΔG°) was calculated from Equation (4) at each temperature tested and is shown in Table 1. The negative values of ΔG° at all temperatures studied confirm the feasibility of the process and the spontaneous nature of adsorption [18].

Here, the positive value (75 kJ mol^{-1}) of the enthalpy change (ΔH°) suggests the endothermic nature of adsorption. Entropy, as the measure of randomness of the system, also indicates the positive value (0.31 kJ K^{-1} mol^{-1}) which suggests an increase in the disorderness during adsorption process. The result is consistent with those reported for the adsorption of fluoride on waste mud [19], Fe-Sn bimetal oxide [20] and adsorption of uranium on *Citrobactor freudii* [21] from aqueous solution.

The relationship between the concentration of BF_4^- after adsorption and the adsorbent dosage in the case of the feed concentration of 4.5 mg dm^{-3} was also investigated. The results show that increasing the adsorbent dosage (up to 1.0 g dm^{-3}) resulted in a rapid decrease in the concentration of BF_4^- remains in the solution and reached zero at 1.0 g dm^{-3} after adsorption. Hence, complete removal of BF_4^- from aqueous solution can be achieved even at trace concentration.

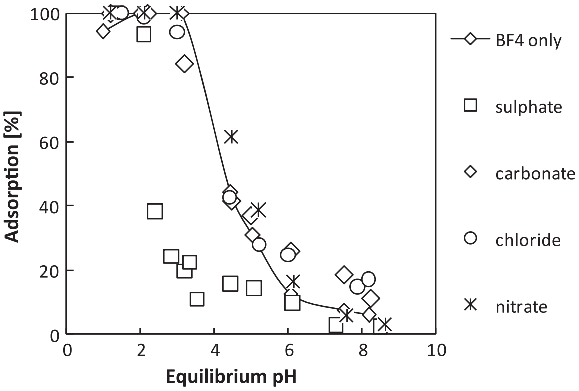


Figure 5. Effect of competitor ions on the adsorption of BF_4^- on Zr(IV)-SOJR. Conditions: volume of solution = 10 cm^3; dry weight of Zr-SOJR added = 10 mg; shaking time = 24 h; temperature = 303 K; concentration of BF_4^- = 10 mg dm^{-3}; concentration of co-existing ions = 100 mg dm^{-3}.

3.5. *Effect of competitor anions*

The adsorption of BF_4^- in the presence of excess concentration of foreign anions such as Cl^-, SO_4^{2-} and NO_3^- is shown in Figure 5 at varying pH. It is evident that the adsorption of BF_4^- on Zr-SOJR is insignificantly influenced by these coexisting anions apart from SO_4^{2-}, which appears to slightly influence the adsorption of BF_4^-.

3.6. *Proposed mechanism of BF_4^- adsorption*

It is evident from Figure 2 that BF_4^- was strongly adsorbed on Zr-SOJR at pH 1–3 whereas it was poorly adsorbed at alkaline pH. This suggests the possibility of elution of BF_4^- using an alkaline solution and also that the adsorption mechanism of BF_4^- on Zr-SOJR may be interpreted as shown in Scheme 2. That is, in the loading of Zr(IV) ion on SOJR, the carboxyl group on SOJR forms a stable five-membered chelate with Zr(IV) ion coordinated with the oxygen atom of the pyranose ring of pectic acid. In this case, all the positive charges of zirconium(IV) (+4) are not completely neutralized by the negative charges of carboxylic groups (−1) due to large steric hindrance of pectic acid. Some of positive charges are neutralized by anionic species existing in aqueous solution – hydroxyl ions in particular. It is inferred that BF_4^- ions are adsorbed on Zr(IV) ions substituted for these hydroxyl ions by a ligand exchange reaction. In addition, since Zr(IV) ions tend to be extensively polymerized and hydrolyzed even at very low concentration to be converted into tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ and octanuclear $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species [22], many hydroxyl ions as well as water molecules are coordinated with Zr(IV), providing a large number of adsorption sites for BF_4^-.

4. Conclusions

This study demonstrated that an agricultural by-product, orange waste, can be used to remove BF_4^- from aqueous solution by loading Zr(IV) ion. Batch wise experiments were performed to investigate the adsorption as a function of pH, contact time, feed concentration and temperature. The optimum adsorption of BF_4^- was observed at pH 2–3. The results of adsorption isotherms suggested that the adsorption equilibrium can be interpreted using the Langmuir model in the studied concentrations range at all temperatures tested. Trace concentrations of BF_4^- can be successfully removed from the aqueous solution even under conditions where large amount of competitor ions coexist (but not sulphate). The positive value (75 kJ mol^{-1}) of the enthalpy change ($\Delta H°$) suggests the endothermic nature of reaction and the positive value (0.31 kJ K^{-1} mol^{-1}) of the entropy change ($\Delta S°$) indicates an increase in randomness in the solid-solution interface during the adsorption of BF_4^- on Zr-SOJR.

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