

RESEARCH ARTICLE

SYNTHESIS OF A NEW ZINC OXIDE MODIFIED CHROMIUM OXY (HYDROXIDE) FOR THE EFFECTIVE REMOVAL OF FLUORIDE FROM DRINKING WATER

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*Key words:-*Chromium (oxy) hydroxide, Defluoridation, Adsorption isotherms, Kinetic model. ZnO_2 modified chromium oxy (hydroxide) (ZOCOH) has been prepared by environment friendly sol-gel method. ZOCOH demonstrated efficient (94.8%) fluoride removal capacity within pH range of 5.0-7.0. Kinetic and equilibrium study reveals that fluoride adsorption by the adsorbent follow the pseudo second order kinetic model. The result of desorption and reuse experiments indicated that the adsorbent could be employed promisingly for reduction of fluoride from drinking water.

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Introduction:-

In developing countries, fluoride contamination in drinking water is a major problem which draws global attention [1]. It is be noted that more than one-third people all over the world are suffering from various diseases like dental and skeletal fluorosis [2, 3]. Excess fluoride intake causes various problems such as fluorosis, skeletal deformities, metabolic disorder in soft tissues and collagen in addition to the fluoride interference in DNA synthesis [4]. World Health Organization (WHO) guideline suggests 1.5 mg L^{-1} as the maximum acceptable fluoride concentration in drinking water [5, 6]. Quite a number of techniques available for removal of fluoride from drinking water includes electro-coagulation [7], precipitation [8], adsorption [9, 10] reverse osmosis [11], and Nalgonda process [12]. However, various factors such as cost, operational and maintenance procedure, etc, limit the use of available technologies. Adsorption techniques affords feasibility and sustainability in rural areas constituting small community mainly because of easy operation procedure and economical factor [13, 14]. Different adsorbents such as activated carbon [15], rare earth oxides [16], and low-cost adsorbents [17] (e.g., bone charcoal, calcite, clay charcoal, tree bark, saw dust, rice husk, ground nut husk), have been investigated for defluoridation. In this aspect, activated carbon is a potential material for the removal of fluoride from drinking water [15]. However, cost factor as well as removal capacity of carbon which varies considerably limit its efficient use for all practical purposes [18, 19]. Attempts are also in progress to develop other suitable materials using activated carbon [18, 20], chromium hydroxide (hydrated carbon) which were also developed and tested for defluoridation of drinking water using batch and column methods [21 - 23].

Use of zinc in fluoride removal gains importance due to various reasons. Zinc dioxide is an efficient sorbent which is insoluble in water and also not so hazardous in nature. Studies conducted by Sivasankar *et al.* [24]

Shown the efficiency of zinc dioxide coated earthen-wares as efficient material for the removal of fluoride from drinking water. As indicated in the literature survey, several other studies have also shown interest in the use of combination of zinc oxide with chromium and other materials for the efficient removal of fluoride. Noted examples

Corresponding Author:- Dr. Nilakantha Dash. Address:- Department of Chemistry, Panchayat College, Dharamgarh, Odisha, India. include use of ZnO_2 coated carbon [25, 26], MnO_2 incorporated bentonite clay, ZnO_2 coated activated carbon [27], $KMnO_4$ - modified activated carbon [28] and hydrated oxides of zinc ores [29] are finding usefulness in fluoride removal.

In this context, present investigation reports preparation of a zinc oxide modified chromium oxide hydroxide (ZOCOH). Hence, defluoridation capacity of the material was evaluated by using batch technique with variation of solution parameters. Further, various kinetic and equilibrium parameters including isotherm equations were also evaluated and compared in order to find the potential application of material for domestic and commercial application purposes.

Materials And Methods:-

Materials and Methods:-

All chemicals used were of analytical grade (E. Merck, India). Double distilled water was used in all experiments. A 1000 mg L^{-1} fluoride stock solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride in 1000 mL of deionized water in a volumetric flask. All other standards and required fluoride concentrations were prepared by serial dilution of the stock solution. The total ionic strength adjustment buffer (TISAB) was prepared according to recommended procedure [21, 29]. Thus, 57.0 mL of glacial acetic acid, 58.0 g of sodium chloride, 7.0 g of sodium citrate and 2.0 g of EDTA (ethylene diamine tetra acetic acid) were dissolved in 500 mL of deionized water. The pH of the solution was adjusted to 5.3 using 5M sodium hydroxide solution.

A pH/ISE meter (Orion model, EA-940 Expandable Ion Analyzer) equipped with combination fluoride selective electrode (Orion Model, 96-09) was employed for the determination of fluoride concentration in samples and standard solutions. The pH was measured with pH/ION meter (WTW Inolab pH/ION Level 2, Germany) using pH glass electrode. The fluoride ion selective electrode was calibrated prior to the measurements of fluoride concentration in samples during each experiment in order to determine the slope and intercept which in turn used to convert potential response to concentration using the following equation:

 $C_{F_{-}} = 10^{(E-const.)/S}$ $\tag{1}$

Where C_F is free fluoride concentration, E is potential, S is the slope of the calibration curve and constant is its intercept. To check the performance of the electrode, particularly in the concentration range of interest, it was initially calibrated using five standards of fluoride solutions ranging from 0.3 mg L⁻¹ to 20 mg L⁻¹. The calibration standard curve is furnished in Fig-1. The slope of the electrode (-58.8 mV/dec) is found to be in the acceptable range (-56.0 mV/dec to -60.0 mV/dec) as shown in Table-1.

Preparation of chromium oxide hydroxide and chromium oxide:-

Hydrated chromium sulfate $(Cr_2(SO_4)_3.14H_20)$ was used for the preparation of chromium hydroxide. 100 g of hydrated chromium sulfate was added to 500 mL of deionized water with continuous stirring using a magnetic stirrer until dissolution was completed. The pH of the resulting solution was measured to be 2.7 which further adjusted to pH of 7.0 using 2 M NaOH. The precipitated material (chromium hydroxide) was separated and dried in an oven for 12 h at 50^oC. Then the same material was placed in a furnace (Calbolite, ELF Model, Waglech International Ltd., UK) at 300^oC for 1 h in order to produce chromium oxi(hydroxide) [30 - 32].

Preparation of zinc oxide modified chromium oxi(hydroxide) (ZOCOH):-

Chromium oxi(hydroxide) was crushed and used as a base material for the preparation of zinc oxide modified chromium oxy(hydroxide) (ZOCOH) hybrid sorbent. The adsorbent was prepared in two steps: In the first step, mixture of 50 mL solution containing 4.58 g of $MnCI_2.H_20$ and 0.5 mL of 10 M NaOH was poured over 50 g of chromium oxy (hydroxide) in a heat resistance dish, and the mixture was heated to $150^{\circ}C$ for 5 h in an oven. In the second step, the same mixture was again heated at $500^{\circ}C$ for 3 h using a furnace. Thus, a dark color zinc dioxide was obtained on the surface of chromium oxy (hydroxide) material.

A series of hydbrid sorbent was also prepared by varying the amount of zinc oxide in zinc oxide modified chromium oxi(hydroxide). Thus, the amount of $ZnCl_2H_2O$ in the mixture was varied (*i.e.*, by addition of 8.88 g, 13.69 g, 19.09 g, and 25.24 g o $ZnCl_2$. H₂O) in order to obtain 11.0%, 16.0%, 21.0% and 26% zinc oxide in ZOCOH sorbent. The prepared sorbent material was washed with deionized water and dried in an oven.

(2)

(3)

Batch Adsorption Studies:-

The adsorption studies for fluoride removal from drinking water by the adsorbent material were carried out in batch process. A 50 mL fluoride solution of desired concentration was taken into PVC conical flask to which a known weight of adsorbent was added and kept for specified time period in a horizontal rotary shaker (shaking speed 200 r.p.m.). Adsorbent was then separated by filtration and the filtrate was analyzed for residual fluoride concentration using ion selective electrode. All adsorption experiments were carried out at room temperature $(20 \pm 2)^{\circ}$ C, except for the case where temperature variation is a parameter. The pH of the solution was adjusted using either HCl or NaOH. All the measurements were made in triplicates and average values are reported. The defluoridation capacity and percentage of adsorption at a given time under specified conditions were determined using the following equations.

% Adsorption (efficiency) = $[(C_o - C_t) C_o] \ge 100$ Defluoridation capacity = $(C_o - C_t)/m$ (mg F/g of sorbent) Where, C_o = initial fluoride concentration in mg L⁻¹ C_1 = concentration of fluoride at time t in mg L⁻¹ m = adsorbent dose in g L⁻¹

Variation of proportion of zinc oxide to chromium oxi(hrdroxide):-

To investigate the effect of varying proportion of zinc oxide on the defluoridation efficiency, materials were prepared with variation of percentage of ZnO_2 . Thus six different materials were obtained containing 0%, 6%, 11%, 16%, 21% and 26% of zinc oxide. Subsequently, 4.0 g L⁻¹ of each adsorbent mixed with 20 mg L⁻¹ fluoride solution for a contact time of 3 h. Based on initial adsorption capacity, the adsorbent with 11% zinc oxide in ZOCOH was further selected for all studies.

Results and Discussion:-

Sorption Studies:-

Variation of adsorbent Dose:-

To investigate the effect of dose and contact time, experiments were conducted by varying adsorbent doses in the range between 0.8 and 4.8 g L^{-1} using initial fluoride concentration of 20 mg L^{-1} and contact time of 3 h (Fig.2). It was observed that with increasing adsorbent dose, the percentage of fluoride adsorption also increases. This is attributed to the fact that higher amount of adsorbent provides greater number of adsorption site [33]. However, the overall capacity decreases with increasing adsorbent dose which may be attributed to the gradual decreases in concentration of fluoride in the solution.

Variation of pH:-

The pH of the solution is an important parameter that controls the adsorption at the water-adsorbent interfaces. In the present case, experimental studies were conducted with initial fluoride concentration of 20 mg L⁻¹ and adsorbent dose of 4.0 g L⁻¹ by varying the initial solution pH from 3 to 10. pH of the solution was adjusted to the desired level with either 0.1 M HCl or 0.1 M NaOH. It was observed that the adsorption of fluoride increases with an increase in pH of the medium (Fig.3). Maximum removal of fluoride (94.8%) could be possible at pH 5.8 However, with further increase in pH of the medium, the amount of fluoride removal further decreases. This could be attributed to the increase in surface negativity of the adsorbent material [34].

Variation of contact time and variation of Dosage:-

Variation of both contact time and amount of adsorbent represents important parameters in evaluating material efficiency with reference to material – anion interaction. The graphical plot of variation of time with different adsorbent dose is presented in Fig.4. The material was quite efficient in removal of fluoride. However, with increase

in adsorbent dose (g L^{-1}), more amount of fluoride could be efficiently removed. To better understand the kinetics of adsorption process by the adsorbent material, two different kinetic models i.e. (i) the pseudo second-order model and (ii) intra-particle diffusion model [35] were used.

The pseudo-second order model is based on the assumption that chemical sorption or chemisorption is one the factors controlling the sorption kinetics [36]. The model is expressed mathematically as:

(4)

 $t/q_t = 1/K_s (q_e)^2 + t/q_e$

where, K_s is the rate constant for pseudo-second order reaction (g mg⁻¹ min⁻¹). q_e and q_t are the amounts of solute sorbed at equilibrium and at any time 't' (mg g⁻¹), respectively. The straight line plot of $t/q_t vs$ t for the kinetic data gives the values for q_e and k_s , respectively, from the slope and intercept. On further simplification, Eqn. (4) can be rewritten as:

$$h = K_a q_e^2$$
⁽⁵⁾

where 'h' is the initial sorption rate (mg g^{-1} min⁻¹)

The theoretical background for the intra-particle mass transfer diffusion model was developed by Weber and Morris [36]. The intra-particle diffusion model is expressed as:

 $q_t = K_i t^{1/2} + C \tag{6}$

Where, K_i is the intra-particle diffusion constant (mg g⁻¹ min^{-1/2}) and C is intercept. The value of K_i is determined from the slope of the plot $q_t vs t^{1/2}$. The value of intercept C provides information about the thickness of boundary layer i.e., the resistant to the external mass transfer.

The result of pseudo-second order kinetic model is illustrated in Fig.5. Table 2 shows rate constants, rate equations and correlation coefficients of pseudo-second order plot of the three different initial concentrations of fluoride (10, 20 and 40 mg L^{-1}) with different material loading. However, it is observed that the rate constants for all the three initial concentrations range of fluoride were very close to each other. So the result indicates that the reaction is described very well by pseudo-second order reaction model [17, 29, 37].

For testing the intra-particle diffusion model, the graphical plot of the amount of fluoride adsorbed (q_t) versus the square root of time ($t_{1/2}$) is shown in Fig.6. In the particular case where the plot of q_t versus $t_{1/2}$ produce a straight line that pass through the origin, then it suggests that the intra-particle diffusion contributes predominantly in the rate-determining step [38]. However, if the data reveal multi-linear regions, it is expected that other mechanisms are also involved along with intra-particle diffusion. Thus, in the present case, as shown in Fig.6, three different regimes can be identified. The first, sharp portion of the curve (observed within $t^{1/2}$ of 5 min) corresponds to the external surface adsorption stage or instantaneous adsorption stage. The second portion of the curve (observed within $t^{1/2}$ of 5 – 12 min) indicates the intra particle diffusion, which is the predominant rate-controlling process. Under this condition, the diffusive transport of fluoride ions occurs through the internal pores of the adsorbent. At low bulk concentration of fluoride ($t^{1/2} > 12$ minutes), the third regime becomes more dominant. In this model, the adsorbent is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ions must diffuse prior to adsorption. In the graphical representation (Fig.6), the linear portion of the curve does not passes through the origin indication the complex nature of the adsorption process. This unusual behavior is possibly due to the heterogeneous nature by both the adsorbent. Therefore, it can be well concluded that the adsorption of fluoride on to ZOCOH is influenced by both surface reactions as well as intra particle diffusion processes.

Variation of solution Concentration:-

To investigate the effect of initial fluoride concentration, experiments were conducted by taking initial fluoride concentrations of 5, 10, 15, 20 and 25 mg L^{-1} using constant adsorbent dose of 4.0 g L^{-1} . Other experimental conditions were set as follows: (i) contact time period of 120 minutes and volume of the solution 50 mL. It was observed that with increase in initial concentration of fluoride, adsorption increases. The result, presented graphically in Fig.7, shows a gradual increase in adsorption capacity which could be due to the availability of both surface area as well as coordination sites in the material.

Isotherm experiments were conducted to investigate the relationship between the solid phase concentration and liquid phase concentration of fluoride ion at equilibrium condition under constant temperature. Isotherm experiments were conducted using adsorbent dose of 4.0 g L^{-1} with varying initial fluoride concentration at constant pH of 7.0. The equilibrium data were fitted to three different adsorption isotherm models such as Langmuir, Freundlich and D-R isotherms [39, 40]. The nature of isotherms can be helpful in contributing to the material surface properties as well as the sorption mechanisms of material – anion interaction [41].

The Langmuir adsorption model is primarily based on monolayer adsorption onto a homogeneous surface. Langmuir model is also based on the assumption that adsorption forces are similar to the forces in chemical interactions [41]. The linearized form of Langmuir equation can be represented by following equation:

$$1/q_{\rm e} = (1/K_{\rm L}q_{\rm m}) (1/C_{\rm e}) + 1/q_{\rm m}$$
⁽⁷⁾

Where, q_e is the amount of fluoride adsorbed at equilibrium (mg g⁻¹), C_e is the equilibrium concentration (mg L⁻¹), q_m is the mono-layer adsorption capacity (mg g⁻¹) and K_L is the Langmuir constant related to the free adsorption energies (L mg⁻¹). The value of q_m and K_L can be calculated, respectively, from the slope and intercept of the linear plot of $1/C_e vs 1/q_e$.

$$\ln q_e = \ln K_F + l/n \ln C_e \tag{8}$$

The linearized form of D-R isotherm can be represented as:

$$\ln q_e = \ln q_m - K\epsilon^2 \tag{9}$$

Where, ε^2 is the Polanyi potential which is equal to RT ln (1 + 1/C_e). q_e is the amount of adsorbate adsorbed at equilibrium per unit of adsorbent (g g⁻¹), q_m is the theoretical saturation capacity (g g⁻¹), C_e is the equilibrium solid concentration (g L⁻¹). K is the constant related to adsorption energy. R is the gas constant and T is the temperature in Kelvin. The value of K and q_m, respectively, is obtained from the slope and intercept of the plot q_e vs ε^2 .

Thus, in the present case, Fig.8 shows Langmuir isotherm model fitting for the experimental data. The result of the Langmuir isotherm model shows that the experimental data is well fitted to the model with a correlation coefficient (R^2) greater than 0.97. The maximum sorption capacity corresponding to complete monolayer coverage was found to be 18.62 mg F⁻ g⁻¹ and the constant K_L, related to adsorption intensity, was found to be 0.383 L mg⁻¹.

The application of Freundlich model to the experimental data is furnished in Fig.9 and various experimental parameters along with correlation coefficients are furnished in Table-3. The result indicated that the experimental fluoride adsorption data also fitted to this model with the correlation coefficient of 0.9529, suggesting that the average energy of adsorption is decreasing with increasing adsorption density with a minimum adsorption capacity of 4.48 mg g⁻¹ and adsorption intensity (n) of 1.67. Thus, the value of n found to be within 1 and 10 indicating Freundlich faborable sorption [39]. The increase in equilibrium fluoride removal capacity with residual fluoride concentration observed indicated the heterogeneous nature of adsorbent surface which is characteristics of adsorption following Freundlich isotherm model fit.

Through both the Freundlich and Langmuir isotherm models are widely used, these models have limitation about elucidating adsorption mechanism property. Therefore, to develop the mechanism of adsorption process, the equilibrium data was tested with the Dubinin-Radushkevich isotherm (D-R isotherm) model. Dubinin-Radushkevich model predicts the sorption nature of the adsorbate on adsorbent and it is used to calculate the mean free energy of sorption.

Fig. 10 shows the D-R isotherm plot for the adsorption of fluoride on to ZOCOH. The correlation coefficient, R^2 value found to be 0.9644, which confirmed the applicability of adsorption process to the model. The sorption

Capacity evaluated from this model is 99.87 mg g⁻¹. From the magnitude of E, the type of adsorption such as chemical sorption or physical sorption can be determined. If the value of E ranges from 1.0 to 8.0 kJ mol⁻¹, sorption could be attributed to the physical adsorption process and if the value ranges from 9.0 to 16.0 kJ mol⁻¹, then the adsorption is attributed to chemical adsorption process [42]. Thus in the present case, the mean free energy of adsorption [E] was found to be 9.71 kJ/mol, which implies that the adsorption is predominantly chemical in nature. This result is in agreement in relation to proposed reaction mechanism, in discussion under the pH effect, as an ion exchange reaction which is chemical in nature.

Log C _F -	-0.523	0	0.699	1	1.301
Potential	2.54 ± 2.48	-28.43 ±2.48	-69.43 ±2.66	-87.53 ±1.94	-104.40 ±2.96
(mV)					

Table 1:- Potential (mV) value as a function of Log C_{F} -

Table 2:- Pseudo-second order rate constants, rate equations, correlation coefficients and their averages for the three different initial fluoride concentration of same loadings

Initial F ⁻ con. and adso. dose	k_2 (g mg ⁻¹ min ⁻¹)	Rate equation	\mathbb{R}^2
10 mg/L F with 1 g/L dose	2.1976 x 10 ⁻²	$t/q_t = 0.5976 + 0.1146t$	0.9999
20 mg/L F with 2 g/L dose	3.6695 x 10 ⁻²	$t/q_t = 0.3579 + 0.1077t$	0.9998
40 mg/L F with 4 g/L dose	4.5396 x 10 ⁻²	$t/q_t = 0.2893 + 0.1040t$	0.9998
	2.4622		
Average	3.4689 x 10 ⁻²	$t/q_t = 0.4138 + 0.1088t$	0.9998

Table 3:- Summary of Freundlich, Langmuir and Dubinin-Radushkevish isotherm model constants and correlation coefficients for adsorption of fluoride.

Isotherm	Constants		Correlation
model			coefficient (R ²)
	b (L/mg)	$q_m (mg/g)$	
Langmuir			0.9712
	0.20244	10.00	
	0.38344	18.62	
Freundlich	$K_F(mg/g)$	n	
			0.9529
	4.48177	1.67	
Dubinin-Radushkevich	$q_s (mg/g)$	E (kJ/mol)	0.9644
(D-R)			
	99.87	9.71	



Fig. 1:- Calibration curve for fluoride concentration measurement (Data for triplicate measurements).



Fig.2:- Adsorption capacity and % F⁻ removal as a function of adsorbent dose, Initial F⁻ concentration 20 mg L⁻¹; contact time: 120 min; pH 7.0 \pm 0.20

Desorption Studies

In order to test the efficacy of the material for reuse and regeneration, fluoride adsorption was performed with 4.0 g L^{-1} dose of material. The other parameters such as time of contact, initial fluoride concentration of solution, volume of solution and pH were set as 120 min, 20 mg L^{-1} , 100 mL and 7.0, respectively. Residual concentration of fluoride in the filtrate was measured to determine the amount of fluoride on the adsorbent. The oven dried used adsorbent material was treated with 100 mL of 0.1%, 0.5% and 1.0% NaOH solutions. The results of desorption of fluoride under various concentrations of NaOH and different conditioning durations are indicated in Fig. 11. It can be seen from the result that desorption was highest in 1% NaOH after 3 h which was 86.2%. Further, the regenerated adsorbent was subjected to reuse and the adsorption efficiency was found to be 82.1% during first cycle of operation suggesting that the adsorbent can be reuse. Initial results of desorption and re-adsorption is quite encouraging however, further studies are required for optimization of result which is underway.



Fig. 3:- Effect of initial solution pH on fluoride removal efficiency and capacity, Initial F⁻ concentration: 20 mg L⁻¹; adsorbent dose: 4.0 g L⁻¹; contact time: 120 min.



Fig. 4:- Variation of contact time at different doses of ZOCOH; initial fluoride concentration: 20 mg L^{-1} ; initial solution pH: 7.0 ± 0.20



Fig. 5:- Pseudo-second order plot of fluoride adsorption kinetics on the adsorbent each with initial fluoride concentrations of 10, 20 and 40 mg L^{-1} with variation of adsorbent doses of 1.0, 2.0 and 4 g L^{-1} , respectively; pH: 7.0 ± 0.20, contact time = 10 h



Fig.6: Intra-particle diffusion model: Adsorption capacity (mg g^{-1}) as a function of square root of time (min)^{1/2}.



Fig.7:- Fluoride removal efficiency at different initial fluoride concentrations; adsorbent dose: 40 g L^{-1} ; pH: 7.0 ± 0.20; contact time: 120 min



Fig. 8:- Linear plot of Langmuir isotherm; adsorbent dose: 4.0 g L⁻¹, contact time: 4 h, pH: 7.0 ± 0.20



Fig.9:- Linear plot of Freundlich isotherm; adsorbent dose: 4.0 g L⁻¹, contact time: 4 h, pH: 7.0 ± 0.20



Fig 10:- Dubinin-Radushkevich isotherm; adsorbent dose: 4.0 g L^{-1} , contact time: 4 h; pH: 7.0 ± 0.20⁰C.



Fig. 11:- Percentage of fluoride desorbed with different concentrations of NaOH solution after 1 h and 3 h; adsorbent dose: 4.0 g L⁻¹, pH: 7.0

Conclusion:-

In this study, the fluoride adsorption capability of a new zinc oxide modified chromium oxi(hydroxide) has been demonstrated. Variation of dose, concentration and pH of the medium affect the uptake of fluoride significantly. The adsorbent was found to be very efficient in removing fluoride in a pH range of 5.0 to 7.0. The adsorption isotherm fitted well to both Langmuir isotherm model and then fitted to the Freundlich isotherm model in the concentration range studied during the experiment. Examination of adsorption data also showed that the Dubinin-Radushkevich isotherm model also provides description of the data very well for the concentration range studied. The adsorption process has energy value of 9.71 kJ mol⁻¹ for fluoride ions, indicating the adsorption process is predominantly chemisorptions process. Kinetic studies showed that the adsorption of fluoride on the adsorbent was well described by pseudo second order reaction model. Further, adsorption of fluoride on the adsorbent takes place through both surface adsorption as well as intra-particle diffusion effect. Investigation of desorption showed that about 86.20% of fluoride could be desorbed in 3 h time interval using 1% NaOH. The material also showed regeneration and reuse capacity in a cycle of operation indicating the possibility of reusing the adsorbent. Thus, zinc oxide modified chromium oxi(hydroxide) represent a promising material with reasonable defluoridation performance which could be considered as a suitable adsorbent for a sustainable solution for the fluoride problem.

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