

## Effects of Cationic Ligands Addition in Hydrous Titanium Oxide on Fluoride Removal Efficiency in Aqueous Medium

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**Abstract:** Complete removal of fluoride from water is still a serious challenge and sustainable removal of fluoride in drinking water is urgently required for the benefit of human kind. In the present study, modified titanium dioxides such as TiO<sub>2</sub>-Cu, TiO<sub>2</sub>-Ca, TiO<sub>2</sub>-Mg and TiO<sub>2</sub>-Fe cationic ligands were prepared by co-precipitation and sol-gel method. The batch adsorption experiment process was used to study the applicability of modified titanium dioxides to remove fluoride from aqueous solutions. All modified titanium dioxides showed higher sorption capacity for fluoride when compared to unmodified titanium dioxide. The Ca, Cu, Mg and Fe with titanium dioxide exhibited a synergistic effect in the cationic adsorbents for fluoride sorption. The effect of different concentrations of Ca, Cu, Mg and Fe ligands on sorption capacity was investigated for 5 h duration. The results obtained clearly showed about 62.25, 62.25, 81.5 and 99.9 % adsorption capacity of fluoride by modified titanium dioxides such as TiO<sub>2</sub>-Cu, TiO<sub>2</sub>-Ca, TiO<sub>2</sub>-Mg and TiO<sub>2</sub>-Fe respectively for 5 h contact time. Modified titanium dioxides such as TiO<sub>2</sub>-Mg and TiO<sub>2</sub>-Fe showed highest fluoride adsorption capacity than TiO<sub>2</sub>-Cu, TiO<sub>2</sub>-Ca, pure TiO<sub>2</sub> (63.25%). The Langmuir isotherm model indicated higher correlation coefficients and provided better agreement with the results obtained. The adsorption kinetic is a chemi-physorption process that follows the pseudo second-order kinetic model.

**Keywords:** Fluoride; Titanium dioxide; Cationic ligand; Adsorption; Sustainable; Langmuir isotherm.

### 1. Introduction

Fluoride, the thirteenth most abundant element in the earth's crust, is the ionic form of the element fluorine [1]. Of all the elements in the periodic table, it is the most reactive. The high electronegativity explains the reactivity of fluorine. It is not an essential element for the living and non-living things to survive. But, its minor concentration is essential for the survival of the species. Fluorspar, cryolyte, and fluorapatite are the most common minerals in which fluoride concentration is at its most [2]. Occurrence and concentration of fluoride in water resources, surface water, and groundwater depends on several attributing factors such as pH, total dissolved solids, alkalinity, hardness, and geochemical composition of aquifers [3-4]. Nowadays, ground water is one of the major sources of drinking water in rural areas, and the most important problem that we are facing today is the occurrence of high fluoride concentration in ground water. As per the WHO report, 20 percent of the fluoride affected villages in the whole world are in India. From the study conducted by Singh et al., it is estimated that there are 33,211 fluoride affected villages in India [5]. In India, high concentration of fluoride in drinking water was first detected in the groundwater of Nellore, Andhra Pradesh in 1937 [6]. The Bureau of Indian Standards (BIS) has recommended 1.0 mg/l as desirable and 1.5 mg/l as

permissible limit for fluoride concentration in drinking water. Where, WHO has prescribed the guideline value for fluoride concentration in drinking water as 1 and 1.2 mg/l for warm and cold climatic regions of the world respectively [7]. The epidemiological studies reveal that drinking water is the major source of fluoride intake [8] and the presence of naturally occurring fluorides or added fluoridated salts in drinking water allows its easy entrance in the body via the gastrointestinal tract [9]. Besides drinking water, fluoride can also enter into the human body through food, industrial exposure, drugs, cosmetics, etc. Though small amount of it is beneficial for human health for preventing dental carries, it is very harmful when it exists in excess of 1 ppm. Dental fluorosis and skeletal fluorosis are the worst scenarios caused by intake of water, which are high in fluoride concentration. Higher concentration of fluoride causes respiratory failure, fall of blood pressure, and general paralysis. Loss of weight, anorexia, anemia, wasting and cachexia are some among the common findings in chronic fluoride poisoning. Continuous ingestion of nonfatal dose of fluoride causes permanent inhibition of growth [10]. Different techniques are available for the removal of fluoride from the aqueous solutions. On the basis of their mode of operation, it is classified into three major groups, viz. chemical method, ion-exchange process, and adsorption method. Adsorption has been reported as a simple, economically viable technique for the removal of fluoride from aqueous solutions [11-12]. Recently, a number of adsorptive materials have been reported for the removal of fluoride from aqueous solutions such as modified cellulose fiber [13], polymer/bio-polymer composites [14], Fe<sub>2</sub>O<sub>3</sub> magnetic nanocomposites [15], bauxite [16], waste iron

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oxide [17], zeolite [18], hydrous bismuth oxide [19] and hydrous ferric oxide [20]. **Table 1** shows the advantages and

disadvantages of fluoride removal technologies, which are still up to day in use [3, 21-26].

**Table1** Comparison of fluoride removal technologies

Technology	Advantages	Disadvantages
Coagulation/precipitation: <i>calcium hydroxide; aluminum hydroxide</i>	High efficiency; commercially available chemical	Expensive, efficiency depends of pH and presence of co-ions in water, adjustment and readjustment of pH is required, elevated residual aluminum concentration, formation of sludge with high amount of toxic aluminum fluoride complex and high amount of retained water (sludge dewatering is required prior disposal)
Membrane filtration: <i>reverse osmosis; nanofiltration</i>	High efficiency; remove other contaminants	High capital high running and maintenance costs toxic waste water produced
Electrochemical treatments: <i>dialysis; electro-dialysis; electro-coagulation</i>	High efficiency; high selectivity	High cost during installation and maintenance
Ion-exchange: <i>Strong basic anion-exchange resin with quaternary ammonium functional groups</i>	High efficiency	Expensive, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate, etc.), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH-dependent
Adsorptive materials: <i>activated alumina; activated carbons; other natural and synthetic adsorbents</i>	Greater accessibility, low cost, simple operation, availability of wide range of adsorbents	High efficiency often demand adjustment and readjustment of pH, some common water ions can interfere fluoride adsorption

The aim of the present study is to prepare modified titanium dioxide by adding suitable cationic ligands under sol-gel technique for the potential fluoride removal from aqueous media and to evaluate fluoride adsorption kinetics by Langmuir isotherm model.

## 2. Materials and Methods

### 2.1. Preparation of titanium oxides with cationic ligands

Titanium dioxide (TiO<sub>2</sub>) was prepared using titanium tetrachloride (TiCl<sub>4</sub>; M.W 189.679 g/mol) using Sol-gel technique for the potential removal of fluoride contents in aqueous media. About 25 ml of TiCl<sub>4</sub> was dissolved in 100 ml of diluted hydrochloric acid (5%) deionized water with continuous stirring using magnetic stirrer (600 rpm) under alkaline condition (pH= 8-12). The obtained homogeneous mixture was kept for aging under darkness for 24 h and it was continuously washed using deionized water to remove chlorine ions from the mixture. Further, the homogeneous mixture of TiO<sub>2</sub> precipitation was dried under the room temperature. In order to prepare cationic ligand embedded titanium dioxide, salts of Ca, Mg, Cu, and Fe were added to TiO<sub>2</sub> powder using deionized water separately with continuous stirring for 24 h. To evaluate the effect of cationic ligand weight ratios in TiO<sub>2</sub> on removal efficiency of fluoride, cationic ligands concentrations were varied as 0.01, 0.05, and 0.1 M. Further, the resultant products were washed continuously using deionized water to remove excess

chlorine contents and dried at 120 °C using pre-heated dust free hot air oven.

### 2.2. Fluoride adsorption experiments

Fluoride removal efficiency of TiO<sub>2</sub> with cationic ligands was carried out in batch experiments using model fluoride solution (10 ppm) under room temperature. A known dose of cationic ligands added TiO<sub>2</sub> powder was added into 100 ml model fluoride solution and allowed for sorption processes for 5 h. Same experimental procedure was followed for the remaining cationic ligands added TiO<sub>2</sub> and a set of blank experiments was maintained without adding adsorbents. The fluoride concentration was determined before and after addition of cationic ligands added TiO<sub>2</sub> by Spadans method [27] using UV-Vis spectrophotometer at 540 nm (Shimadzu, UV 1800). Aqueous mixtures of fluoride along with adsorbents were stirred in every one hour interval and after a fixed duration, aqueous solution was filtered through Whatman No. 42 filter paper. The filtrate was analyzed for the remaining fluoride content and the fluoride removal efficiency of cationic ligands added TiO<sub>2</sub> was calculated using Eq. 1:

$$\text{Fluoride removal capacity (\%)} = \frac{C_0 - C_i}{C_0} \times 100 \quad (1)$$

Where, C<sub>0</sub> and C<sub>i</sub> are the initial and final concentration of fluoride in solution (mg/L) respectively.

The effect of adsorbent dose and contact duration on the fluoride removal efficiency of cationic ligands added TiO<sub>2</sub> was studied by varied concentration of adsorbent and contact time. The adsorption isotherms and kinetics of the removal of fluoride using cationic ligands added TiO<sub>2</sub> was studied by Langmuir isotherm model [28] to correlate the results obtained.

### 3. Results and Discussions

**Table 2** Theoretical parameters for Langmuir isotherm model fitted on experimental data of fluoride sorption on modified TiO<sub>2</sub>.

Sl.No	Sample combination	q <sub>max</sub> (mg/g)	K <sub>L</sub> (l/mg)
1	TiO <sub>2</sub>	0.896	3.193
2	TiO <sub>2</sub> -Ca(0.01M)	0.0602	3.909
3	TiO <sub>2</sub> -Ca(0.05M)	0.539	5.719
4	TiO <sub>2</sub> -Ca(0.1M)	0.915	3.373
5	TiO <sub>2</sub> -Cu(0.01M)	0.517	4.393
6	TiO <sub>2</sub> -Cu(0.05)	0.771	2.682
7	TiO <sub>2</sub> -Cu(0.1M)	0.469	6.325
8	TiO <sub>2</sub> -Mg(0.01M)	0.709	3.785
9	TiO <sub>2</sub> -Mg(0.05M)	0.985	0.714
10	TiO <sub>2</sub> -Mg(0.1M)	0.359	5.377
11	TiO <sub>2</sub> -Fe(0.01M)	0.805	2.819
12	TiO <sub>2</sub> -Fe(0.05M)	1.969	0.285
13	TiO <sub>2</sub> -Fe(0.1M)	1.342	0.313

Contamination of fluoride in waters from various sources is one of the serious problems that the world is facing today. Potential and modified titanium dioxide based adsorbents such as Ti-Cu, Ti-Ca, Ti-Mg and Ti-Fe were prepared through sol-gel technique for the removal of fluoride contents in aqueous media. The results showed that significant removal of fluoride content by modified titanium dioxide based adsorbents even in the presence of coexisting chloride, nitrate, and sulfate ions. Previous research studies have reported that about 80 to 98.80 % fluoride ions removal efficiency using different modified TiO<sub>2</sub> adsorbents [29].

#### 3.1. Adsorption Isotherm

One of the important applications of adsorption in industrial area is modelling equilibrium sorption. It yields data that expedite designing and optimizing the process [30]. In this study, to fit experimental data Langmuir isotherm model was selected. Irving Langmuir in 1916 developed the Langmuir isotherm to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. Langmuir isotherm is given by the following equation;

$$C_e / q_e = 1 / K_L \cdot q_{\max} + C_e / q_{\max} \quad (2)$$

Where, q<sub>e</sub> = equilibrium metal ion concentration on the adsorbent (mg/g); C<sub>e</sub> = equilibrium metal ion concentration

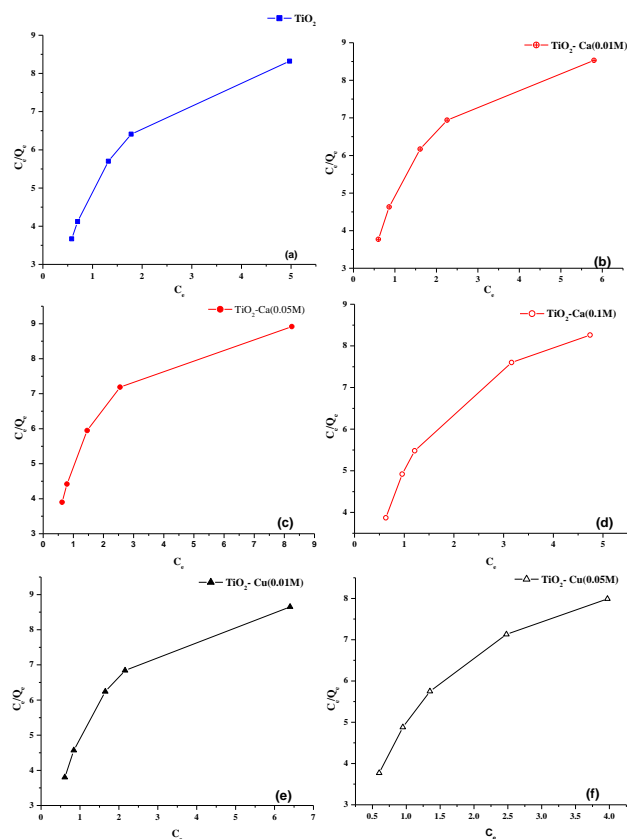
in the solution (mg/l); q<sub>max</sub> = maximum adsorption capacity of adsorbent (mg/g); K<sub>L</sub> = Langmuir adsorption constant (l/mg).

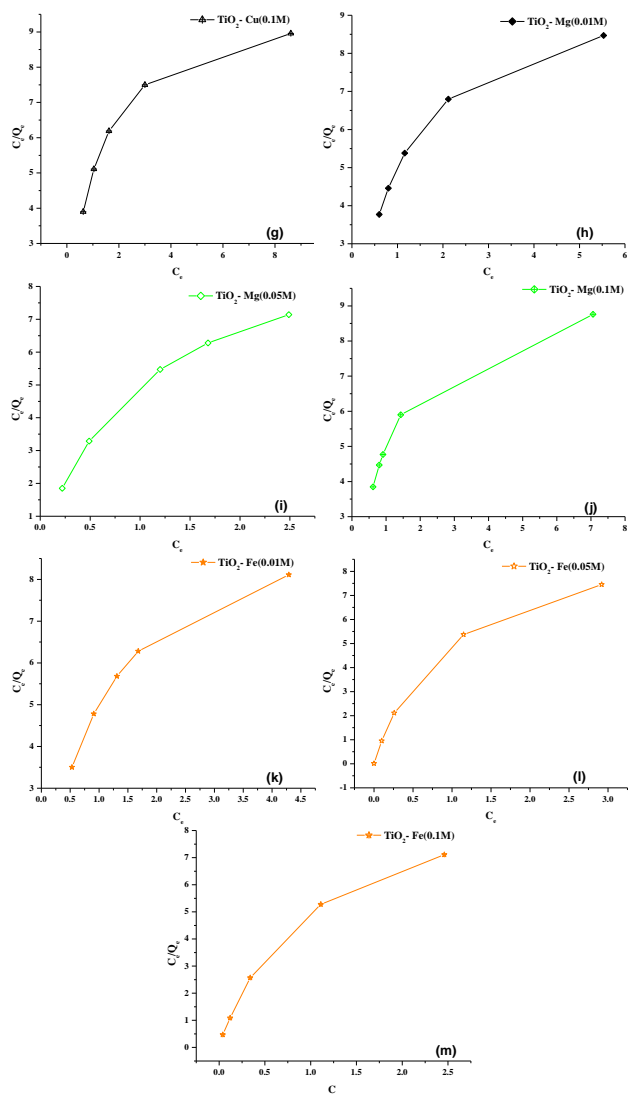
The values of Langmuir constants q<sub>max</sub> and K<sub>L</sub> were calculated from the slope and intercept of the linear plot of C<sub>e</sub>/Q<sub>e</sub> versus C<sub>e</sub>.

**Table 2** lists the Langmuir adsorption constants calculated from linearized form of the corresponding isotherms with their coefficients of determination.

#### 3.2. Adsorption Kinetic

To determine the design of reactor and optimization of process for a successful practical application, the rate of metal sorption has to be determined [31]. **Figure 1** shows the removal efficiency of fluoride by modified titanium dioxide as a function of time. The results divulge that a gradual increase in adsorption efficiency with increasing contact time. The plausible reason may be due to large number of vacant binding sites, which are available for adsorption. The rapid kinetics has significant importance in practical application, as it will facilitate small reactor volumes ensuring high efficiency and economy [32].





**Figure 1** Effect of contact time on sorption of fluoride by (a) pure TiO<sub>2</sub>; (b) TiO<sub>2</sub>-Ca(0.01M); (c) TiO<sub>2</sub>-Ca(0.05M); (d) TiO<sub>2</sub>-Ca(0.10M); (e) TiO<sub>2</sub>-Cu(0.01M); (f) TiO<sub>2</sub>-Cu(0.05M); (g) TiO<sub>2</sub>-

Cu(0.10M); (h) TiO<sub>2</sub>-Mg(0.01M); (i) TiO<sub>2</sub>-Mg(0.05M); (j) TiO<sub>2</sub>-Mg(0.10M); (k) TiO<sub>2</sub>-Fe(0.01M); (l) TiO<sub>2</sub>-Fe(0.05M); (m) TiO<sub>2</sub>-Fe(0.1M)

The results obtained from kinetic experiments were analyzed using pseudo first-order [33] and pseudo second-order [34] kinetic models. The pseudo first-order kinetic model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time [35]. The linear form of pseudo first order is generally expressed as Eq. 3:

$$\log (q_e - q_t) = \log q_e - K_{1,ads} * t / 2.303 \quad (3)$$

Where,  $q_t$  (mg/g) = amount of metal ion adsorbed at time  $t$  (min);  $q_e$  = amount of metal ion adsorbed at equilibrium (mg/g);  $K_{1,ads}$  = constant of pseudo first-order kinetic model ( $\text{min}^{-1}$ ).

The values of  $K_{1,ads}$  and  $q_e$  can be obtained from the slope and intercept of the plot of  $\log (q_e - q_t)$  versus  $t$  respectively.

The pseudo second-order kinetic model is based on the assumption of chemisorption of the adsorbate on the adsorbent [36]. The linear form of this model is given in Eq. 4 as:

$$t / q_t = 1 / K_{2,ads} * q_e^2 + t / q_e \quad (4)$$

Where,  $K_{2,ads}$  is the constant of pseudo second-order kinetic ( $\text{g mg}^{-1}\text{min}^{-1}$ ). The values of  $K_{2,ads}$  and  $q_e$  can be calculated from the slope and intercept of the plot of  $t / q_t$  versus  $t$ . The values of the parameters along with coefficient of determination for each model are tabulated in **Table 3**.

**Table 3** Parameter values calculated using the pseudo first-order and pseudo second-order models for the adsorption of fluoride by modified titanium dioxides.

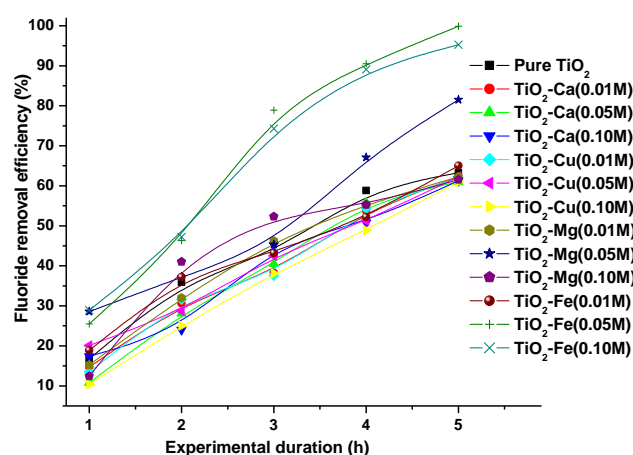
Sl.No	Modified titanium dioxides	$q_{exp}$ (mg/g)	First-order kinetic model		Second-order kinetic model	
			$K_{1,ads}$ ( $\text{min}^{-1}$ )	$q_{eq}$ (mg/g)	$K_{2,ads}$ ( $\text{g mg}^{-1}\text{min}^{-1}$ )	$q_{eq}$ (mg/g)
1	TiO <sub>2</sub>	3.67	$31.88 \times 10^{-2}$	1.061	$3.9 \times 10^{-2}$	3.71
2	TiO <sub>2</sub> -Ca (0.01M)	3.77	$23.57 \times 10^{-2}$	0.961	$32.4 \times 10^{-3}$	3.56
3	TiO <sub>2</sub> -Ca (0.05M)	3.9	$31.6 \times 10^{-2}$	1.101	$59.8 \times 10^{-3}$	4.1
4	TiO <sub>2</sub> -Ca (0.1M)	3.87	$22.34 \times 10^{-2}$	0.918	$46.8 \times 10^{-3}$	3.51
5	TiO <sub>2</sub> -Cu (0.01M)	3.8	$24.93 \times 10^{-2}$	0.983	$15.3 \times 10^{-3}$	4.25
6	TiO <sub>2</sub> -Cu (0.05)	3.77	$19.74 \times 10^{-2}$	0.866	$8.6 \times 10^{-2}$	3.59
7	TiO <sub>2</sub> -Cu (0.1M)	3.9	$20.16 \times 10^{-2}$	0.94	$44.3 \times 10^{-3}$	4.64
8	TiO <sub>2</sub> -Mg (0.01M)	3.77	$27.83 \times 10^{-2}$	0.994	$2.3 \times 10^{-2}$	3.95
9	TiO <sub>2</sub> -Mg (0.05M)	1.85	$17.83 \times 10^{-2}$	0.967	$86.4 \times 10^{-3}$	2.12
10	TiO <sub>2</sub> -Mg (0.1M)	3.85	$30.44 \times 10^{-2}$	0.95	$16.4 \times 10^{-3}$	4.21
11	TiO <sub>2</sub> -Fe (0.01M)	3.5	$17.75 \times 10^{-2}$	0.832	$86.8 \times 10^{-3}$	3.92
12	TiO <sub>2</sub> -Fe (0.05M)	0.01	$31.02 \times 10^{-2}$	1.24	$9.8 \times 10^{-3}$	0.15
13	TiO <sub>2</sub> -Fe (0.1M)	0.47	$34.59 \times 10^{-2}$	1.26	$28.9 \times 10^{-3}$	0.63

**Table 4** Adsorption capacity and other parameters for the removal of fluoride in aqueous media using different adsorbents

Adsorbent	Adsorption capacity	Concentration range	Contact time (min)	pH	Temperature (°C)
Acid treated spent bleaching earth	7.752 mg/g	5-45 mg/dm <sup>3</sup>	30	3.5	-
Hydroxyapatite	4.54 mg/g	2.5x10 <sup>-5</sup> to 6.34x10 <sup>-2</sup> mg/L	-	6	-
Fluorspar	1.79 mg/g				
Activated quartz	1.16 mg/g				
Calcite quartz	0.39 mg/g				
Basic oxygen furnace slag	4.58-8.07 mg/g				
Alum sludge	5.394 mg/g	5-35 mg/L	240	6	32
Activated alumina( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> )	0.86 mmol/g	15-100 mg/L	384-1440	5-6	30
Activated alumina(OA 25)	1450 mg/kg	2.5-14 mg/L	-	7	-
Metallurgical grade alumina	12.57 mg/g	-	-	5-6	20
La(III) impregnated alumina	0.350 mM/g	2 mM/l	1200	5.7-8	25
Alum-impregnated activated alumina	40.68 mg/g	1-35 mg/L	90	6.5	25
MnO coated alumina	2.851 mg/g	2.5-30 mg/L	90	7±0.2	30±2
Hydrous MnO coated alumina	7.09 mg/g	10-70 mg/L	120	5.2	25
Copper oxide-coated alumina	7.770 mg/g	10 mg/L	1440	-	30±1
Magnesia-activated alumina	10.12 mg/g	5-150 mg/L	180	6.5-7	30±1
Calcium oxide-modified activated alumina and MnO modified activated alumina	101.01 mg/g and 10.18 mg/g	1-1000 mg/L	2880	5.5	25
Alkoxide-origin alumina	2 mg/g	0-25 mg/L	1440	7	30±2
Quick lime	16.67 mg/g	10-50 mg/L	75	-	25±2
Anhydroxide impregnated limestone	43.10-84.03 mg/g	100 mg/L	300	8	25
Schwertmannite	50.2-55.3 mg/g	10-90 mg/L	1440	3.8	30-22.6
Modified TiO <sub>2</sub> -Fe (0.05 M)	9.99 mg/g	10 mg/L	300	7	28
Modified TiO <sub>2</sub> -Mg (0.05 M)	8.15 mg/g	10 mg/L	300	7	28
Modified TiO <sub>2</sub> -Ca (0.10 M)	6.13 mg/g	10 mg/L	300	7	28
Modified TiO <sub>2</sub> -Cu (0.05 M)	6.23 mg/g	10 mg/L	300	7	28

The results clearly indicated that the coefficient of determination of pseudo second-order model was higher in comparison to pseudo first-order model and the calculated experimental value of  $q_e$  was close to that for pseudo second-order kinetic model [28]. This suggests that the pseudo second-order kinetic model fitted the adsorption kinetic data of fluoride onto modified titanium dioxides better than the pseudo first-order kinetic model. In accordance with pseudo second-order kinetic model, the rate-limiting step of this sorption system may be chemisorption involving Valency forces through sharing or exchanging electrons between adsorbent and adsorbate [37]. Since, fluoride is an anion; therefore, it was assumed that the addition of the cations such as Ca, Mg, Cu, Fe can enhance the removal through the attraction forces among opposite charged species in aqueous solution [7]. This consisted with results taken from the pseudo second-order model that the chemisorption may be the rate-limiting step. Modified TiO<sub>2</sub> with different cationic ligands clearly showed higher removal efficiency of fluoride when compared with the previously reported materials [38-52] and fluoride

removal efficiency of different adsorbents is tabulated in **Table 4**.



**Figure 2** Fluoride removal efficiency (%) of (a) pure TiO<sub>2</sub>; (b) TiO<sub>2</sub>-Ca(0.01M); (c) TiO<sub>2</sub>-Ca(0.05M); (d) TiO<sub>2</sub>-Ca(0.10M); (e) TiO<sub>2</sub>-Cu(0.01M); (f) TiO<sub>2</sub>-Cu(0.05M); (g) TiO<sub>2</sub>-Cu(0.10M); (h)



TiO<sub>2</sub>-Mg(0.01M); (i) TiO<sub>2</sub>-Mg(0.05M); (j) TiO<sub>2</sub>-Mg(0.10M); (k) TiO<sub>2</sub>-Fe(0.01M); (l) TiO<sub>2</sub>-Fe(0.05M); (m) TiO<sub>2</sub>-Fe(0.1M)

Chloride salts of Ca and Cu did not influence the adsorption capacity of TiO<sub>2</sub> and they exhibited the removal efficiency, which was almost equal to that of pure TiO<sub>2</sub>. TiO<sub>2</sub> with Mg and Fe showed significant removal of fluoride in aqueous solution (**Figure 2**). To check the effect of concentration of cationic ligands in fluoride adsorption, we prepared three different concentrations of each cationic ligand. In the case of Ca and Cu, removal efficiency decreased with increase in concentration of cationic ligands due to the attribution of high dissociation and precipitation rate of CaCl<sub>2</sub> and CuCl<sub>2</sub> in aqueous media [53]. Moreover, increased concentration of CaCl<sub>2</sub> in aqueous media could make effect on cationic ligand formation with TiO<sub>2</sub> due to rapid precipitation rate of Ca salts in aqueous media [54]. In the case of TiO<sub>2</sub> with Mg and Fe, the removal efficiency increased with concentration to a particular limit and after that the removal efficiency decreased with increase in concentration due to rapid precipitation rate in aqueous media, which apparently make effect on the cationic ligand formation with TiO<sub>2</sub> [26]. High fluoride removal efficiency was observed in TiO<sub>2</sub>-Fe cationic ligand system because of increased number adsorption sites, which could be attributed to the trivalent nature of dissociated Fe ions into TiO<sub>2</sub> in aqueous media [55]. The removal efficiencies of each cationic ligand were listed as follows.

Ca [0.01M (62.25%) > 0.1M (61.25%) > 0.05M (61%)]  
Cu [0.05M (62.25%) > 0.01M (62%) > 0.1M (61%)]  
Mg [0.05M (81.5%) > 0.01M (62.25%) > 0.1M (61.5%)]  
Fe [0.05M (99.9%) > 0.1M (95.25%) > 0.1M (65%)]

Pure TiO<sub>2</sub> showed removal efficiency of 63.25%, which is 3.6 times less than the removal efficiency of TiO<sub>2</sub> with Fe ligand. Among the four ligands used for the fluoride removal in aqueous media, Fe showed the maximum removal efficiency (99.9%) followed by Mg (81.5%), whereas Ca and Cu showed similar removal efficiency (62.25%).

The removal efficiency in the top order was as follows:

TiO<sub>2</sub>-Fe (0.05M) > TiO<sub>2</sub>-Fe (0.1M) > TiO<sub>2</sub>-Mg (0.05M) > TiO<sub>2</sub>-Fe (0.01M) > TiO<sub>2</sub>

#### 4. Conclusion

Modified TiO<sub>2</sub> with different cationic ligands were prepared through simple soft-chemical technique and they were found to be effective adsorbents for the removal of fluoride from aqueous solution. The results obtained clearly showed that the sorption efficiency was dependent on the concentration of salts used and contact time. TiO<sub>2</sub> modified with Ca (0.1M) and Cu (0.05M) showed less removal efficiency when compared with Mg (0.05M) and Fe (0.05M) solution

exhibited maximum adsorption of fluoride. The study indicated that the TiO<sub>2</sub> modified with Mg (0.05M) and Fe (0.05M) cationic ligands improved fluoride sorption potential with respect to the pure TiO<sub>2</sub>. TiO<sub>2</sub> with Fe (0.05 M) solution gave maximum percentage (99.9) of fluoride removal among the Ca, Mg, Cu, and Fe ligands individually at different concentration levels.

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