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Application of nano aluminum oxide and multi-walled carbon nanotube in fluoride removal

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ABSTRACT

The problem of environmental pollution by nanoparticles, which have recently entered the industrial processes around the world, is very important. This study aimed to determine the optimum condition (pH, initial concentration, and sorbent dosage) for removal of fluoride using multi-walled carbon nanotubes (MWCNTs) and nano aluminum oxide (Al_2O_3). Then, the mortality rate of *Daphnia magna* using Al_2O_3 laden with fluoride and MWCNTs laden with fluoride was investigated under the acquired optimum conditions. The obtained results showed that the highest removal rate of fluoride was 96.9% for Al_2O_3 at pH = 6 and 60.1% for MWCNTs at pH = 5. The lethal concentration-50 (LC_{50}-24 h) was 0.501 g/L for MWCNTs laden with fluoride and 0.475 g/L for Al_2O_3 laden with fluoride. Besides, the LC_{50}-48 h was 1.188 and 1.101 g/L for Al_2O_3 laden with fluoride and MWCNTs laden with fluoride, respectively. The study findings demonstrated that Al_2O_3 laden with fluoride and MWCNTs laden with fluoride had the lowest toxicity and mortality effects on *Daphnia magna*.

Keywords: Nano aluminum oxide; Multi-walled carbon nanotubes; Fluoride; Toxicity; *Daphnia magna*

1. Introduction

Evidence has shown that fluoride pollution in drinking water and environment is a worldwide problem [1–6]. Around the world, fluoride components are discharged into the environment from wastewaters of various industries, including drugs, cosmetics, semiconductor manufacturing, coal power plants, glass and ceramic production, electroplating, rubber, aluminum production, phosphate fertilizers, brick and tile production, drinking water fluoridation, and toothpaste [2,7–9]. Researchers have observed that drinking water with fluoride concentrations greater than 1.5 mg/L could cause dental/skeletal fluorosis, a risk factor for hypertension, changes in DNA structure, and lowering of children's IQ and neurotransmitters in long run [5,8,10–17]. Up to now, different techniques have been developed to remove excessive fluoride from aquatic solutions. These methods include adsorption [2], ion exchange [18], precipitation [19] hybrid sorbent resin [20], magnesium oxide-coated nanoparticles [3], sulfate-doped Fe_3O_4/Al_2O_3 nanoparticles [10], Fe_3O_4–NH_2 [21], nano hydroxyapatite/chitosan [22], aluminum (hydr) oxide coated pumice [11], tartaric acid modified graphene oxide [23], hydrous man-

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ganese oxide-coated alumina [19] carbon nanotube [24,25], granular zirconium iron [26], and other sorbents. Among these methods, adsorption is one of the most dominant ones due to its simplicity and availability of a wide range of adsorbents [2]. Among sorbents, nano-alumina (Al_2O_3) and Multi-Walled Carbon Nanotubes (MWCNTs) are the best because of their low cost, nanosize, high specific surface area, and great mass transfer efficiency [2,27,28]. Furthermore, the increasing use of Paraoxon, Malathion, Deltamethrin, Allethrin, Glyphosate, Lindane, Pb, Cu, Co, Cd, PCBs, lead nitrate, and nanoparticles, such as Al_2O_3, MWCNTs, and nano- and non-nano-scale TiO_2 and ZnO particles, results in excessive inflow of toxic substances mainly into the aquatic ecosystem [29–38]. Therefore, aquatic fauna is affected by the toxic substances that eventually enter the environment [34]. In addition, several species of aquatic fauna are susceptible to deleterious effects when exposed to these pollutants. *Daphnia magna* is valuable as a test organism due to its sensitivity to toxic substances, ease of identification and handling, ubiquitous distribution, and extensive use in toxicity testing [39]. In addition, *Daphnia magna* is fecund and reproduce parthenogenically, which allows establishment of clones with little genetic variability and reproducible testing results [32,35,39]. Moreover, *Daphnia magna* has been widely used as a standard test organism in aquatic toxicology because of its fast growth rate, small size, short life cycle, and amenability to lab culture [32,39].

The present study aims to investigate the effects of pH, initial fluoride concentration, and adsorbent dose on the removal of fluoride from aqueous solution using MWCNTs and Al_2O_3 for acquiring optimum conditions. Using optimum conditions, the mortality rate of *Daphnia magna* on Al_2O_3 laden with fluoride and MWCNTs laden with fluoride was investigated. Hence, lethal concentration-50 (LC_{50}), no observable effect concentration (NOEC), lowest observed effect concentration (LOEC), and lethal concentration-20 (LC_{20}) were also examined for Al_2O_3 laden with fluoride and MWCNTs laden with fluoride using *Daphnia magna* under optimum conditions in 24 and 48 h.

2. Materials and methods

Al_2O_3 and MWCNTs were purchased from US Research Nanomaterials, Inc. Sodium fluoride (NaF) was used to prepare fluoride stock solution. In doing so, fluoride solution 100 mg/l followed by 1, 2, and 3 mg/l solutions were made. In order to determine the optimum conditions, as shown in Table 1, 50 ml water samples containing fluoride, and Al_2O_3 and MWCNTs as absorbents were poured into Erlenmeyer flasks. Then, pH of the samples was adjusted in acidic, basic, and neutral ranges until the effects of several pH levels on fluoride removal were specified. It was found that fluoride was removed at pH = 6 for Al_2O_3 and pH = 5 for MWCNTs. Therefore, first the level of pH was adjusted at the optimum level and then, the samples were placed in the reciprocating shaker model 3018 at different times (5–120 min) and adsorbent dosages (0.2–0.6 g/L) at 250 rpm. Afterwards, the optimum conditions for removal of fluoride were applied at the concentrations of 1, 2, and 3 mg/L. In each experi-

Table 1
The experimental design for both physico-chemical and ecotoxicological assessments

Daphnia magna	Time (min)	pH	Adsorbent dose (g/L)	Initial fluoride concentration (mg/L)	Adsorbent without laded fluoride
NO	5 to 210	4	0.2, 0.3, 0.35, 0.4 and 0.5	1, 2 and 3	MWCNTs ORAl_2O_3
NO	5 to 210	5	0.2, 0.3, 0.35, 0.4 and 0.5	1, 2 and 3	
NO	5 to 210	6	0.2, 0.3, 0.35, 0.4 and 0.5	1, 2 and 3	
NO	5 to 210	7	0.2, 0.3, 0.35, 0.4 and 0.5	1, 2 and 3	
NO	5 to 210	9	0.2, 0.3, 0.35, 0.4 and 0.5	1, 2 and 3	
NO	5 to 210	Optimum	0.2, 0.3, 0.35, 0.4 and 0.5	1	
NO	5 to 210	Optimum	0.2, 0.3, 0.35, 0.4 and 0.5	2	
NO	5 to 210	Optimum	0.2, 0.3, 0.35, 0.4 and 0.5	3	
NO	5 to 210	Optimum	0.2	Optimum	
NO	5 to 210	Optimum	0.3	Optimum	
NO	5 to 210	Optimum	0.35	Optimum	
NO	5 to 210	Optimum	0.4	Optimum	
NO	5 to 210	Optimum	0.5	Optimum	
NO	5 to 210	Optimum	Optimum	Optimum	
NO	Optimum	Optimum	Optimum	Optimum	
Daphnia magna	Time	Optimum pH	Adsorbent dose (g/L)	Optimum fluoride concentration (mg/L)	Adsorbent laded with fluoride
Yes (*n* = 10)	24–28 h	6	0.1–2.6	1	Al_2O_3 laden with fluoride
Yes (*n* = 10)	24–28 h	5	0.1–2.6	1	MWCNTs laden with fluoride

ment, pH of the samples was adjusted, 0.5 g/L Al_2O_3 and MWCNTs were poured in 50 ml of the sample, and the mixture was placed in the shaker at the desired time. After the shaking time, Al_2O_3 and MWCNTs were deposited using a centrifuge and then, fluoride concentration was measured. A spectrophotometer DR/5000 (Method 8029) was utilized to measure fluoride concentration in water.

Finally, bioassay was carried out using *Daphnia magna* according to standard methods. In addition, the desired concentrations (0.1–2.6 g/L) were obtained by detection range tests [34,40–42] and each concentration was studied for 24 and 48 h [43]. On the other hand, different nominal concentrations of the absorbents (0.1–2.6 g/L) were added to fluoride solution 1 mg/l (as the optimum concentration) (Table1). Thus, MWCNTs and Al_2O_3 solution exposed to fluoride was prepared and the experimental bioassay was conducted according to the standard methods [39,43]. *Daphnia magna* was also cultured in 4 L glass jars containing 3 L of reconstituted hard water prepared based on the standardized USEPA protocol [43]. In so doing, *Daphnia magna* was separated in the culture and washed with double deionized water for 3 times in five minutes. Then, *Daphnia magna* was added to test tubes each containing 10 *Daphnia magna* (at the optimum conditions) and control tubes each containing 10 *Daphnia magna* (without MWCNTs and Al_2O_3 laden with fluoride). After 24 and 48 h, the number of dead or immobilized organisms was counted. All materials used in toxicity experiments were initially washed in 10% HNO_3 and rinsed with deionized distilled water [39,40,42,43]. Consequently, the results of *Daphnia* mortality were recorded based on LC_{50}-24 h, LC_{50}-48 h, LC_{20}-24 h, LC_{20}-48 h, LOEC-24 h, LOEC-48 h, NOEC-24 h, and NOEC-48 h [40,42,43]. The obtained data from Probit analysis (SPSS 19) were used in Excel software to plot graphs.

3. Results and discussion

3.1. Effect of pH

To determine the optimum pH level for fluoride removal from aqueous solution by Al_2O_3 and MWCNTs, the experiments were conducted at pH = 4–9. pH was kept at the desired level by 0.1 M HNO_3 or 0.1 M NaOH with 1000 mL of the prepared solution containing 1 mg/L fluoride and 0.5 g/L Al_2O_3 and MWCNTs at the contact time of 5–210 min. As depicted in Fig. 1, the highest adsorption rate of fluoride was 96.9% for Al_2O_3 at pH = 6 and 60.1% for MWCNTs at pH = 5. Hence, pH = 6 and pH = 5 were chosen for assessment of *Daphnia magna* mortality on Al_2O_3 laden with fluoride and MWCNTs laden with fluoride, respectively.

3.2. Effect of adsorbent dose

The experiments were conducted with adsorbent doses (Al_2O_3 and MWCNTs) ranging from 0.2 to 0.5 g/L. The impact of the adsorbents' doses on removal of fluoride has been presented in Fig. 2. The initial fluoride ion concentration was fixed at 1 mg/L, the contact time was kept between 5 and 210 min, and pH was kept at 6 for Al_2O_3 and 5 for MWCNTs. The results demonstrated that the optimum dose of the adsorbents was 0.5 g/L for both Al_2O_3 and MWCNTs. Hence, this dose was chosen for further studies. It should be noted that this dose gave 96.14% and 57.98% fluoride ion removal efficiency for Al_2O_3 and MWCNTs, respectively. Moreover, the removal of fluoride increased with increasing the adsorbents' doses (Fig. 2).

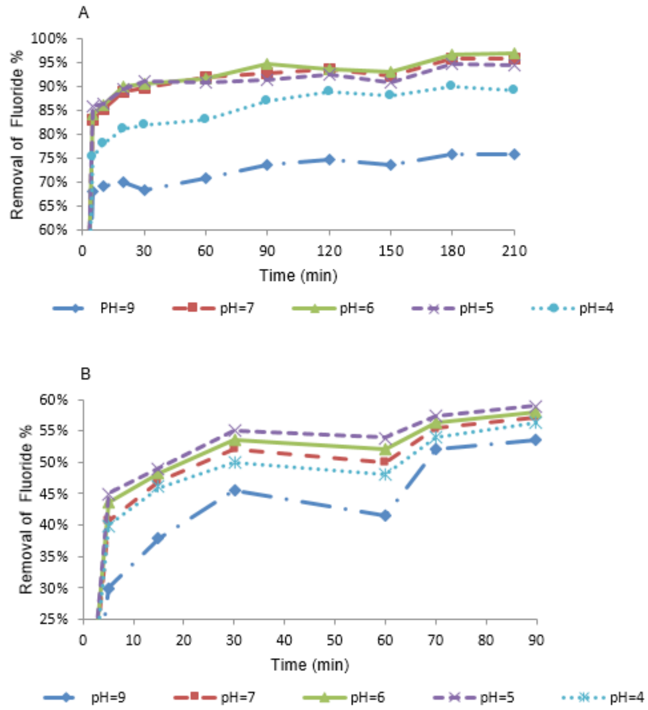

Fig. 1. The effect of pH (Al_2O_3 (a) and MWCNTs (b)) on fluoride removal (fluoride concentration = 1 mg/L, dose of adsorbents = 0.5 g/L, time = 5–210 min, speed = 250 rpm).

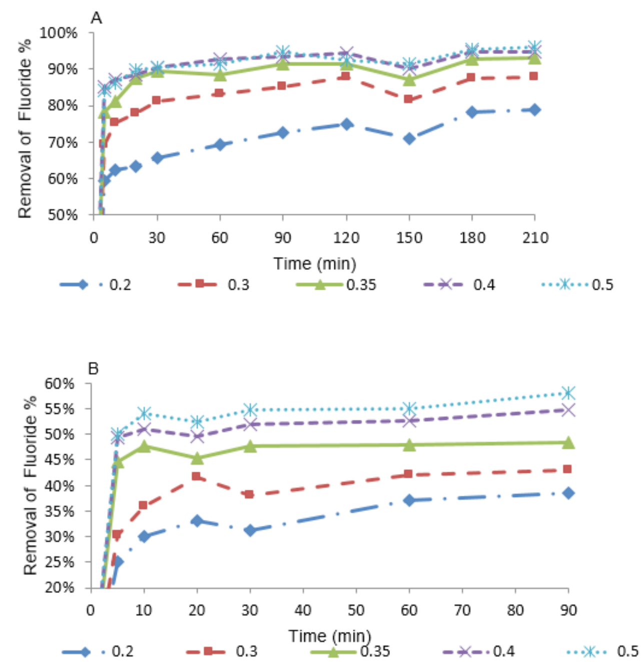

Fig. 2. The effect of adsorbent dose (Al_2O_3 (a) and MWCNTs (b)) on fluoride removal (fluoride concentration = 1 mg/L, pH = 6 for Al_2O_3 and pH = 5 for MWCNTs, temperature = 298°K, time = 5–210 min, speed = 250 rpm).

3.3. Effect of different initial concentrations

In this part, the initial fluoride concentration ranged from 1.0 to 3.0 mg/L, the adsorbent dose was 0.5 g/L, pH was 6 for Al_2O_3 and 5 for MWCNTs, stirring rate was 250 rpm, and contact time ranged from 5 to 210 min at 298°K. The results are shown in Fig. 3. Accordingly, the removal percentage of fluoride ion decreased with increase in the initial fluoride ion concentration because the capacity of the adsorbent is gradually reduced with increase in the initial fluoride concentration. Additionally, the percentage of fluoride ion uptake for Al_2O_3 gradually decreased from 96.9% to 84.2%, 93.9% to 79.1%, and 89.8% to 75% at fluoride ion concentrations of 1 mg/L, 2 mg/L, and 3 mg/L, respectively with increasing time from 5 to 210 min. Also, the percentage of fluoride ion uptake for MWCNTs gradually decreased from 59% to 45%, 52.5% to 30.2%, and 43% to 28.3% at 1 mg/L, 2 mg/L, and 3 mg/L fluoride ion concentrations, respectively with increasing time from 5 to 90 min. This could be attributed to the fact that for a fixed adsorbent dosage, there are limited available adsorption sites that become saturated at a certain concentration. Thus, increase in the initial fluoride ion concentration is accompanied by decrease in its removal percentage. Hence, 1.0 mg/L initial concentration of fluoride laden with the adsorbents was chosen for investigating the mortality rate of *Daphnia magna*.

3.4. Effect of toxicity of MWCNTs and Al_2O_3 laden with fluoride on Daphnia magna

This study examined the effect of toxicity of MWCNTs laden with fluoride and Al_2O_3 laden with fluoride on *Daphnia magna*. In this stage, the toxicity test was performed on *Daphnia magna* at the adsorbent dose of 0.1–2.6 g/L and optimum conditions (pH = 6 for Al_2O_3, pH = 5 for MWCNTs, and fluoride concentration = 1 mg/L). The results are presented in Fig. 4. Our results showed that the NOEC-24 h was 0.501 g/L for Al_2O_3 laden with fluoride and 0.391 g/L for MWCNTs laden with fluoride. Besides, NOEC-48 h was 0.475 g/L for Al_2O_3 laden with fluoride and 0.151 g/L for MWCNTs laden with fluoride. Karin et al. (2009) reported that the NOEC for adult *Daphnia magna* mortality and offspring *Daphnia magna* production by nano- and non-nano-scale TiO_2 and ZnO particles were 30 and 3 mg/L, respectively. Moreover, the NOEC-24 h and NOEC-48 h of phenanthrene-loaded nano-ZnO were 0.4 and 0.12 mg/L, respectively. Additionally, phenanthrene-loaded nano-ZnO had a mortality rate of 100% by *Daphnia magna* at 24 and 48 h at 5 and 4 mg/L concentrations, respectively [40]. According to Fig. 4, LOEC was 0.643 and 0.612 g/L for Al_2O_3 laden with fluoride at 24 h and 48 h, respectively. Besides, these measures were respectively obtained as 0.544 and 0.314 g/L for MWCNTs laden with fluoride. In addition, LC_{20}-24 h was 0.755 g/L for Al_2O_3 laden with fluoride and 0.666 g/L for MWCNTs laden with fluoride. Besides,

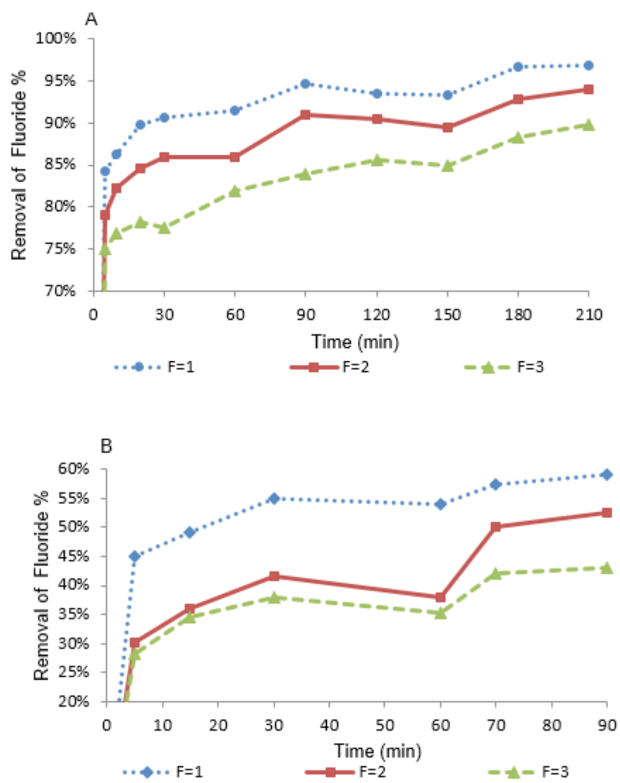

Fig. 3. The effect of initial fluoride concentration on fluoride removal (dose of adsorbents Al_2O_3 (a) and MWCNTs (b) = 0.5 g/L, pH = 6 for Al_2O_3 and pH = 5 for MWCNTs, temperature = 298°K).

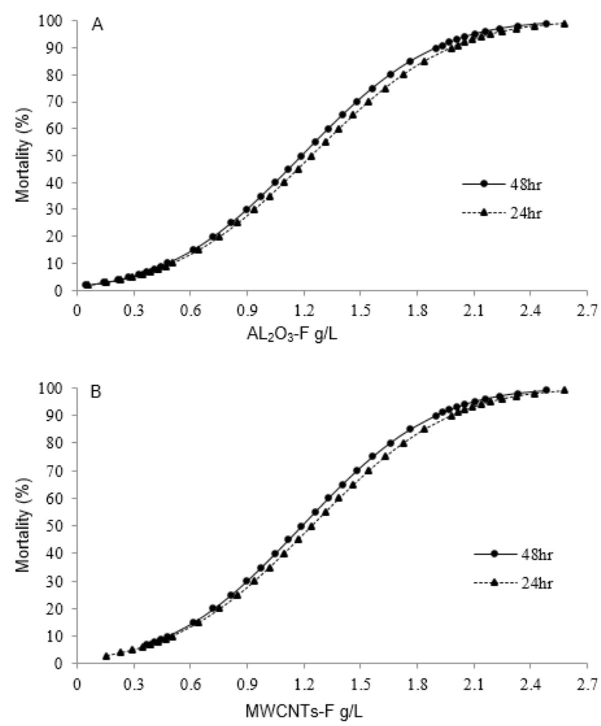

Fig. 4. The effect of toxicity of Al_2O_3 laden with fluoride (A) and MWCNTs laden with fluoride (B) on *Daphnia magna* at 24 and 48 h (fluoride concentration = 1 mg/L, different adsorbent doses, pH = 6 for Al_2O_3 laden with fluoride and pH = 5 for MWCNTs laden with fluoride, temperature = 298°K).

LC_{20}-48 h was 0.720 g/L for Al_2O_3 laden with fluoride and 0.444 g/L for MWCNTs laden with fluoride. Additionally, LC_{50} was 1.240 and 1.188 g/L for Al_2O_3 laden with fluoride at 24 h and 48 h, respectively. These measures were also respectively obtained as 1.193 and 1.101 g/L for MWCNTs laden with fluoride. Thus, the results showed close LC_{50} values for both nano-absorbents in 24 and 48 h (Table 2 and Fig. 4). Hence, Al_2O_3 laden with fluoride and MWCNTs laden with fluoride had no toxic effects on *Daphnia magna*, indicating that they could be used for removal of fluoride from aquatic solutions without any toxicity. This means that although increasing the exposure time and doses of adsorbents exposed to fluoride resulted in a slight increase in the mortality rate, differences in LC_{50} values were very low at 24 and 48 h (Table 2 and Fig. 4). In addition, the high LC50 obtained for Al_2O_3 and MWCNTs laden with fluoride indicated that both nano-absorbents had low toxic effects on *Daphnia magna.* Therefore, toxicity of MWCNTs and Al_2O_3 laden with fluoride does not depend on the exposure time to *Daphnia magna*.

Similarly, Chandra et al. conducted a chronic study using *Daphnia pulex* at 0.25, 0.5, and 1.0 mg/L lead and arsenic solutions in 2007. The results of that study indicated that LC_{50} (48 h) was 4.0 and 3.4 mg/L for lead and arsenic, respectively [44]. In another study using *Daphnia magna*, LC_{50} values of nano-ZnO were 2.6 and 2.1 mg/L at 24 and 48 h, respectively. On the other hand, LC_{50} values of phenanthrene-loaded nano-ZnO were 1.5 and 1.0 mg/L at 24 and 48 h, respectively [40]. In addition, Margit et al. (2008) reported that LC_{50} values for bulk ZnO, nano-ZnO, and $ZnSO_4 \cdot 7H_2O$ using *Daphnia magna* were 8.8, 3.2, and 6.1 mg/L, respectively. They also stated that LC_{50} values for bulk CuO, nano-CuO, and $CuSO_4$ were 165, 3.2, and 0.17 mg/L, respectively [45]. Furthermore, bioassay tests indicated that phenol was toxic on *Daphnia magna* in quite low LC_{50} values [46]. In the present study, the mortality rate of *Daphnia magna* was less than 10% in the control tubes.

Table 2
Cumulative mortality of *Daphnia magna* (*n* = 10 for each concentration) exposed to MWCNTs and Al_2O_3 laden with fluoride

No. of mortalities			No. of mortalities		
Concentration of MWCNTs -F (g/L)	24 h	48 h	Concentration of Al_2O_3-F (g/L)	24 h	48 h
Control	0	0	Control	0	0
0.1	0	0	0.1	0	1
0.35	0	0	0.35	1	1
0.5	1	1	0.5	1	2
1.5	1	2	1.5	2	2
2	2	2	2	2	3
2.6	3	4	2.6	3	5
Toxicity parameters			Toxicity parameters		
NOEC	0.501	0.475	NOEC	0.391	0.151
LOEC	0.643	0.612	LOEC	0.544	0.314
LC_{20}	0.755	0.720	LC_{20}	0.666	0.444
LC_{50}	1.240	1.188	LC_{50}	1.193	1.101

4. Conclusion

The obtained results may be summarized as follows:

- Al_2O_3 removed 96.9% of fluoride at pH = 6 and MWCNTs removed 60.1% of fluoride at pH = 5.
- The NOEC-24 h was 0.501 g/L for Al_2O_3 laden with fluoride and 0.391 g/L for MWCNTs laden with fluoride. Besides, NOEC-48 h was 0.475 g/L for Al_2O_3 laden with fluoride and 0.151 g/L for MWCNTs laden with fluoride.
- The LOEC was 0.643 and 0.612 g/L for Al_2O_3 laden with fluoride at 24 h and 48 h, respectively. These measures were respectively obtained as 0.544 and 0.314 g/L for MWCNTs laden with fluoride.
- The LC_{20}-24 h was 0.755 g/L for Al_2O_3 laden with fluoride and 0.666 g/L for MWCNTs laden with fluoride. Besides, LC_{20}-48 h was 0.720 g/L for Al_2O_3 laden with fluoride and 0.444 g/L for MWCNTs laden with fluoride.
- The LC_{50}-24 h for Al_2O_3 laden with fluoride and MWCNTs laden with fluoride were 1.240 and 1.193 g/L, respectively. LC_{50}-48 h was also 1.188 and 1.101 g/L for Al_2O_3 laden with fluoride and MWCNTs laden with fluoride, respectively.
- The high LC50 obtained for Al_2O_3 and MWCNTs laden with fluoride indicated that both nano-absorbents had low toxic effects on *Daphnia magna.* Therefore, these absorbents could be used for removal of fluoride from aquatic solutions without any toxicity, as tested on *Daphnia magna*.

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