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Studies on Adsorption Behavior of Fluoride on Native Sand Material

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ABSTRACT: Incidences of fluorosis, a disease caused due to consumption of fluoride in high doses, are being reported from all over the globe. Due to its deleterious effects on human health, Fluoride mitigation strategies are among the major concern worldwide. In the same context, the present study was carried out to check the adsorptive behavior of locally available low cost sand materials. The adsorption experiments were carried out in batch mode with two types of sand materials collected from two different locations. The effect of process parameters such as initial fluoride concentration, pH, adsorbent dose and contact time were investigated. The maximum fluoride removal under optimized conditions was calculated. Both type-I and type-II sand materials showed significant adsorption upto 80 and 86% within the range of pH 5-7. The experimental data obtained with type-II sand adsorbents followed both Langmuir and Freundlich isotherm with high correlation value, R^2 = 0.97 & 0.94 respectively but the equilibrium data obtained with type I sand was better fitted to Langmuir model with R^2 = 0.98.

Key Words: Fluoride adsorption, native sand, adsorption isotherm

I. INTRODUCTION

The groundwater at many places in the Indian subcontinent has been found contaminated with various inorganic contaminants, particularly arsenic, fluoride, nitrate, sulphate, iron, manganese and other heavy metals. Some of these pollutants are present naturally in waters as a result of dissolution from underground rocks and sediments in groundwater aquifers and may be acquainted with anthropogenic activities such as industrial waste disposal and agricultural runoff. Elevated levels of these pollutants in water are reducing water quality (Sharma and Walia, 2016; Geeta *et al.,* 2015) and causing multiple health hazards to livestock (Velhal & Kamble, 2010) and humans (Singh *et al,* 2016).

According to the guidelines of WHO, the permissible limit of fluoride concentration in drinking water is 1.5 mg/L (WHO, 2004). Below this value, it prevents dental caries, but the continuous consumption of high concentrations of fluorides in excess of this causes dental and skeletal fluorosis. The other physiological functions affected by high intake of fluoride include degeneration of muscles, deformation in blood cells, low hemoglobin level, metabolic disturbances and organ dysfunctioning of particularly neural and renal systems (Fawell *et al.,* 2006; Yiamouyiannis, 1993 and Xiang *et al.,* 2003)

Several processes are currently available for removal of fluoride such as adsorption, membrane filtration, ion-exchange, electrocoagulation and electrodialysis (Sujana *et al.,* 2009; Hu *et al.,* 2005; Solangi *et al.,* 2009; Sundaram *et al.,* 2009; Kabay *et al.* 2008; Garg and Sharma, 2016). Of these methods, the adsorption process has been most widely accepted and investigated because of its simplicity, versatility, convenience and cost effectiveness.

A wide variety of adsorbents has been employed by various researchers to remove fluoride from water. These include alumina and modified alumina based adsorbents (Das *et al.,* 2005; Mohapatra *et al.,* 2004 and Tang *et al.,* 2009), activated carbon, calcium, iron, metal oxides/hydroxides/oxyhydroxides and metal impregnated metal oxides, natural materials such as coal, clay and zeolite as an adsorbent (Agarwal *et al.,* 2003; Puka, 2004), bio sorbents (Mohan *et al.,* 2007; Jagtap *et al.,* 2009), industrial waste such as red mud, fly ash, waste carbon slurry etc. (Cengeloglu *et al.,* 2002; Lai and Liu, 1996; Piekos and Paslawaska, 1999) and the layered double hydroxides have been tested for the fluoride removal.

Activated alumina has been extensively studied because of its inert nature, safe to use and handle, high capacity attributed to high surface area and porosity and selectivity. However, it exhibits poor defluoridation capacity at neutral pH. Also, the release of aluminum ions into water poses additional health hazards and therefore restricts its use for large scale applications. (Wang *et al.,* 2008; Goswami *et al.,* 2012)

Various earth materials including sand, soils and clays are well known for their remarkable characteristic of being adsorptive as reported in literature. These materials allow water laden with organic and inorganic ions to percolates through and during this course of percolation these ions are removed by these earth materials and only pure water moves down to form the ground water bodies. This adsorptive property of earth materials has been exploited by various researchers for removal of water pollutants. Adsorption of fluoride on sand, clay and soils in their natural and modified form has also been extensively studied. As per literature these adsorbents are reported to have good removal efficiencies. Moreover, these materials are cheap, chemically stable and available in abundance and hence can be exploited as potential adsorbents on large scale applications. (Chidambaram *et al.,* 2003; Kamble *et al.,* 2009; Wang and Reardon, 2001; Elango *et al.* 2010; Wambu *et al.,* 2012)

In the present study, a low cost locally available sand material was selected for removal of fluoride from the aqueous solution. The kinetic of adsorption of fluoride on the sand and the effect of some important parameters such as initial fluoride concentration, pH, adsorbent dosage and contact time on the adsorption onto sand were compared.

II. MATERIALS AND METHOD

The simulated stock solution of 100 mg/L fluoride was prepared by dissolving an appropriate amount of sodium fluoride in deionized water. The working solutions were prepared by making suitable dilutions of stock solutions. All the chemicals used were of analytical grade. The concentration of fluoride before and after adsorption was measured by SPADNs method.

A. Preparation of adsorbent

The two types of sand samples were collected from two different locations, Pathankot and Jira regions of Punjab state of India. Geological formations of both selected areas are older and newer alluvial types deposits of quaternary age, mainly composed of silica and quartz. The adsorbent was first sieved & filtered to obtain grains with size less than 100 µm and were washed several times with the deionized water. Finally the adsorbent was dried in oven at 250°C for 12 hours.

B. Adsorption experiments

Adsorption experiments were carried out in batch mode. All experiments were conducted with 10 mg/L fluoride concentration, contact time between adsorbent and the fluoride solution 10-200 min, pH 1-8. The dosage of the adsorbent was varied between 5-35 g/L at constant temperature 30°C.

In a preliminary analysis, five sets of experiments were conducted in which the fixed amount of adsorbent (20g/L) was added to the 100 ml fluoride solution of concentration 10 mg/L in polyethylene flasks of 250 ml capacity. These were allowed to mix by placing on a shaker set at 180 rpm for 120 minutes. The pH of the solution of each set was adjusted between 1 and 8 (1.5, 2.5, 3.5, 4.5, 5.5, 6.5 and7.5 respectively) by adding small increments of 0.1N HCl and 0.1N NaOH. The adsorption of each set was measured at regular intervals and recorded. The percent fluoride removal was calculated using following equation:

$$Percent\ Removal\ of\ Fluoride = \frac{(Co-Ce)}{Ce} \times 100 \quad ...(1)$$

where Co and Ce are the initial and final concentrations of fluoride in solution.

The effects of other adsorption process parameters such as, fluoride concentration, adsorbent dose and contact time on adsorption were also studied. Under optimized conditions, the adsorption of fluoride on both types of natural sand material was determined and compared. Experimental data obtained was analyzed with classical isotherm models such as Langmuir and Freundlich.

RESULTS AND DISCUSSION

A. Effect of pH

The pH is an important factor that affects the adsorption of fluoride on an adsorbent. It determines the nature and extent of ionization of functional groups present on the surface of adsorbents and thereby affects the overall removal efficiency. In this study, the experiments to investigate the effect of pH were conducted with constant fluoride concentration 10 mg/L and adsorbent dose 20 g/L. The effects of pH on fluoride adsorption by both the adsorbents are shown in Fig. 1.

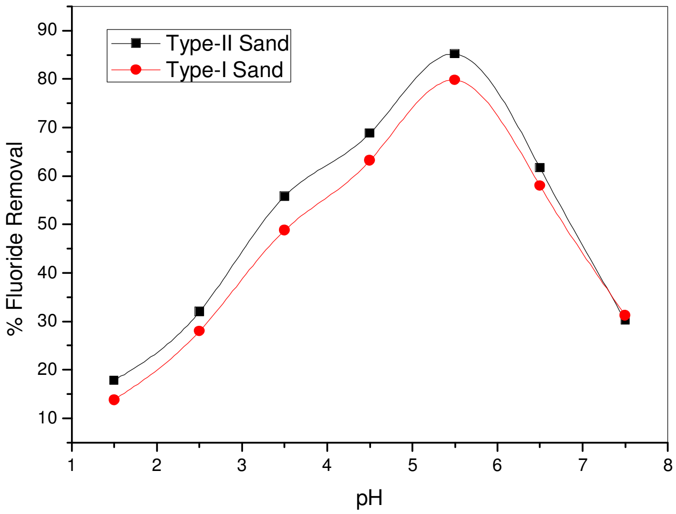

Fig. 1. Effect of pH on percent fluoride adsorption.

Trends of results of fluoride adsorption with pH formed a bell shaped curve with peak at pH 5.5. This is clear from the figure that initially adsorption increased with increase in pH reaching maximum 79.8% and 85.2% respectively with both the adsorbents and then declined drastically with further rise in pH. The 25-30% decrease in adsorption was observed when pH was varied by one unit from peak value in both cases. The increase in adsorption with initial pH was because of the availability of more protonated sites in the low pH range that actually favors the fluoride adsorption. In the acidic medium, the adsorption sites on surface of adsorbent are positively charged and have strong affinity for negatively charged fluoride ions. Similarly fluoride adsorption was very less in the alkaline pH because the surface sites get deprotonated and developed negative charges that in turn repel the fluoride ions. The significant adsorption upto 72-80% and 75-85% was observed between pH 5-6 with both the adsorbents respectively. Therefore, all other sets of experiments were conduct with optimum pH 5.5.

B. Effect of adsorbent dose

The adsorbent dosage is another important parameter that affects the cost of the removal process. The adsorbent with minimal dosage giving maximum fluoride removal are more plausible in terms of cost effectiveness. In this study, the effect of adsorbent dose on adsorption was studied by mixing the varied amount of adsorbents from 5-35 g/L with 100 ml solution of fixed fluoride concentration 10 mg/L at constant temperature for 120 minutes.

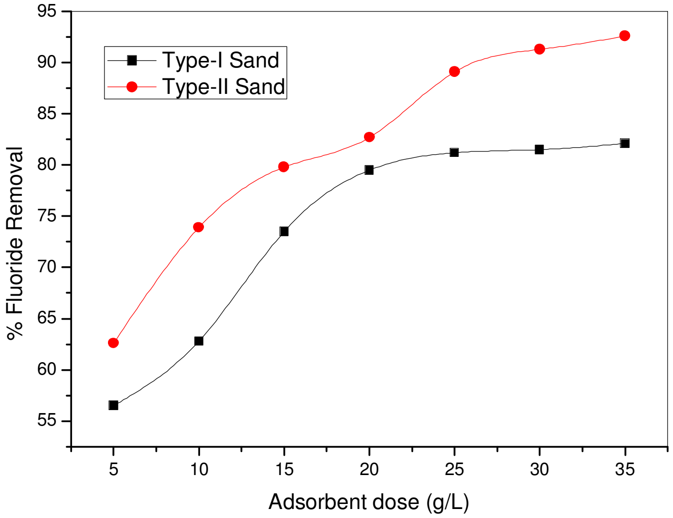

Fig. 2. Effect of Adsorbent Dose on adsorption.

The adsorption was measured at optimized pH with the adsorbents. Similar trends of adsorption with adsorbent dosage were observed with both adsorbents (Fig. 2). From the results presented in Fig. 2, it is clear that with adsorbent dose varied from 5-35g/L, initially the adsorption was increased greatly and was maximum (82.1% and 92.6%) for dosage (35 g/L) with type-I and type-II sand adsorbents. This may be attributed to the increased surface area and binding sites available for the fixed fluoride ions concentration. Very little increase in percent adsorption from 81.2–82.1 and 89.1–92.6 was achieved when adsorbent dose was increased from 25–35 g/L and therefore further experiments were conducted with 25 g of adsorbent as an optimum dosage.

C. Effect of Initial Concentration of Fluoride

To check the effects of fluoride concentration on adsorption, the 2g adsorbent was mixed with the same volume of fluoride solution of varying concentration between 10 to 120 mg/L. The results of fluoride ion concentration on percent fluoride removal are presented in Fig. 3. The adsorption capacity was calculated as per equation 2.

$$Adsorption\ capacity,\ Qe(mg/g) = \frac{Co-Ce}{M} \times \mathrm{V} \quad \text{...(2)}$$

Where Co and Ce are the initial and final fluoride, concentrations (mg/L), M is the mass of adsorbent (grams) and V is the volume of solution (in litres)

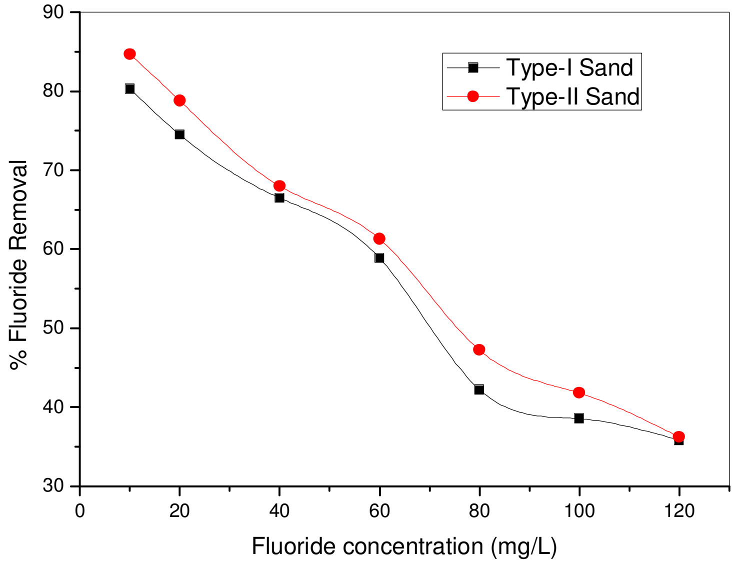

Fig. 3. Effect of Fluoride Concentration on adsorption.

The findings showed that percent adsorption was decreased with increased fluoride concentration. This is because with increasing concentration of fluoride in the adsorption sites on the adsorbent surface become saturated and lesser number of sites were available to accommodate the more fluoride ions. From the table 1, it is clear that although the percent fluoride removal was decreased but the adsorption capacity that represents the actual amount of fluoride adsorbed per unit mass of adsorbent was increased.

Table1: Adsorption capacities of type-I and type-II adsorbents calculated under optimized conditions (pH = 5.5, adsorbent dose = 20 g/L, contact time = 120 mins, stirring speed = 180 rpm) for different fluoride concentrations.

Fluoride concentration (mg/L)	Type-I sand (Qe)	Type-II sand (Qe)
10	0.40	0.42
20	0.74	0.78
40	1.33	1.36
60	1.77	1.84
100	1.98	2.09
120	2.15	2.17

D. Effect of Contact Time

Studies on investigating the effect of contact time on adsorption process was conducted by performing experiments with fixed fluoride concentration, i.e. 10 mg/L under the optimized conditions of pH and adsorbent dose. The contact time was varied between 10-200 minutes and concentration of fluoride remaining in solution was determined at regular intervals. The results of contact time on percent fluoride removal are presented in Fig. 4. The results indicated that initially the fluoride ion was removed at a faster rate in first 90 minutes and gradually turned out to slow and finally became independent after reaching equilibrium. The equilibrium was established in 120 minutes.

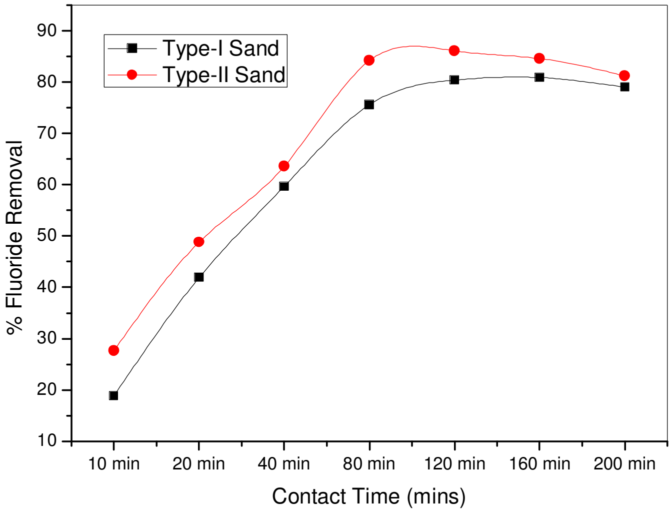

Fig. 4. Effect of Contact Time on adsorption.

E. Adsorption Isotherms

The equilibrium analysis is an important to understand the complex phenomenon of adsorption asit provides valuable information about quantitative performance of adsorption by describing the equilibrium of solute distributed in two different phases; the solid phase representing the adsorbent and solution. In the present study, adsorption data was analyzed with the classical isotherm models viz. Langmuir and Freundlich models to check the fitness of data.

F. Langmuir isotherm

The Langmuir isotherm model is based on assumption that a solute is adsorbed on surface as monolayer with homogenous distribution of adsorption sites. The data obtained was validated as per the linear form of equation represented as:

$$\frac{Ce}{Qe} = \frac{1}{Qo\ b} + \frac{Ce}{Qo} \qquad \ldots(3)$$

Where *Ce* is the fluoride equilibrium concentration (mg/L), *Qe*, the amount of fluoride adsorbed at equilibrium (mg/g), *Qo* represent the maximum amount of ions adsorbed per unit of adsorbent to form complete monolayer on adsorbent and *b* is the sorption equilibrium constant. The value of *b* indicates the affinity of ions to surface binding sites.

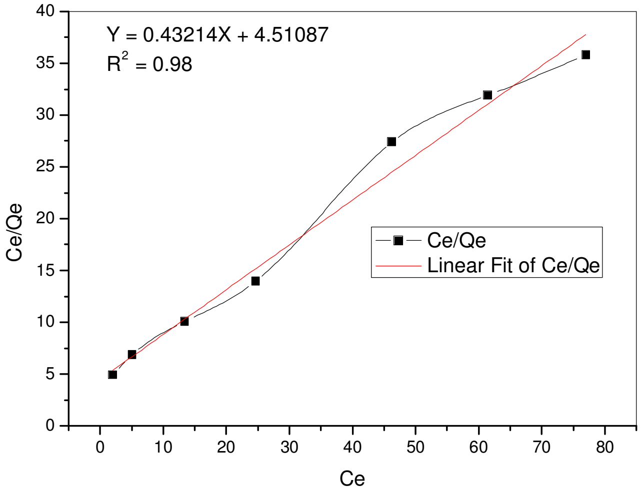

Fig. 5 (a). Langmuir plot of Fluoride adsorption on Type-I sand.

At constant temperature with optimized conditions of pH, adsorbent dose and stirring speed, the experimental data obtained with both type-I and type-II adsorbent followed Langmuir isotherm with high correlation value, R^2 = 0.98 and 0.97. The low value of slope, less than one (0.43 & 0.28 for type-I and type-II adsorbent) indicated that significant adsorption was occurred at lower fluoride concentration.

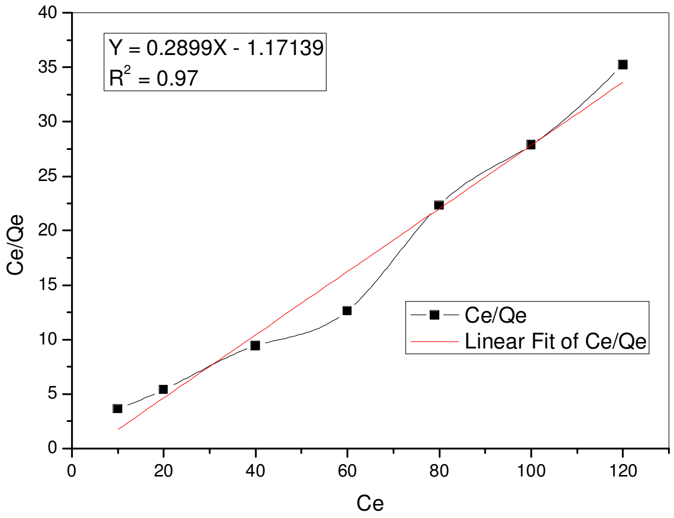

Fig. 5 (b). Langmuir plot of Fluoride adsorption on Type-II sand.

The linear form of Langmuir isotherms of fluoride ions for type-I and ype-II sand adsorbents are presented in Fig. 5 (a) and 5(b).

G. Freundlich isotherm

Freundlich isotherm model is another model extensively used to describe the heterogenous adsorption of solute in multilayers. The model was applied to the adsorption data obtained under optimized set of conditions as per equation 4:

$$\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C \qquad ...(4)$$

where x/m gives amount of fluoride ions adsorbed per unit mass of adsorbent and Ce is again the fluoride ion concentration at equilibrium. The constant K_f gives value of adsorption capacities under defined conditions of pH and adsorbent dose. The plot of log x/m with log Ce for type-I and type-II adsorbents are presented in Fig. 5 (c) and (d).

The data for type-I sand adsorbent obeyed the Freundlich isotherm with correlation value equal to 0.90 whereas the value of R^2 for Langmuir was quiet high (R^2 = 0.98). This suggested that the fluoride adsorption on type-I sand material is best fitted to Langmuir model.

The Freundlich and Langmuir R^2 value for type II sand adsorbent was 0.94 and 0.97 indicated that fluoride adsorption data for type-II sand material was followed both isotherms but the data was little better fitted to Langmuir model.

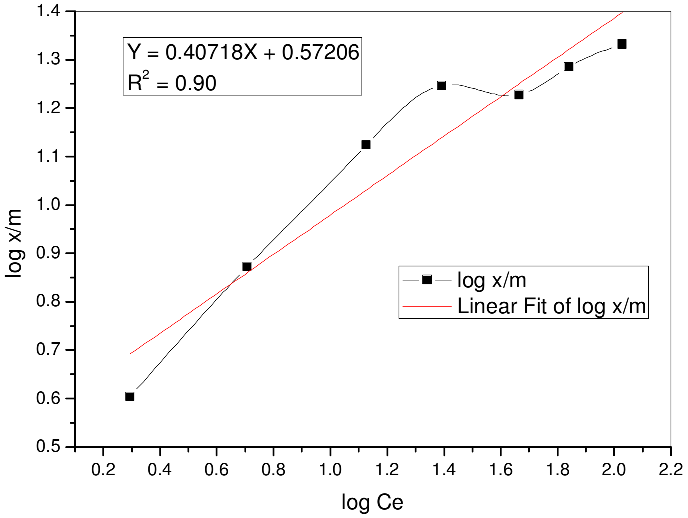

Fig. 5 (c). Freundlich plot of fluoride adsorption on type-I sand.

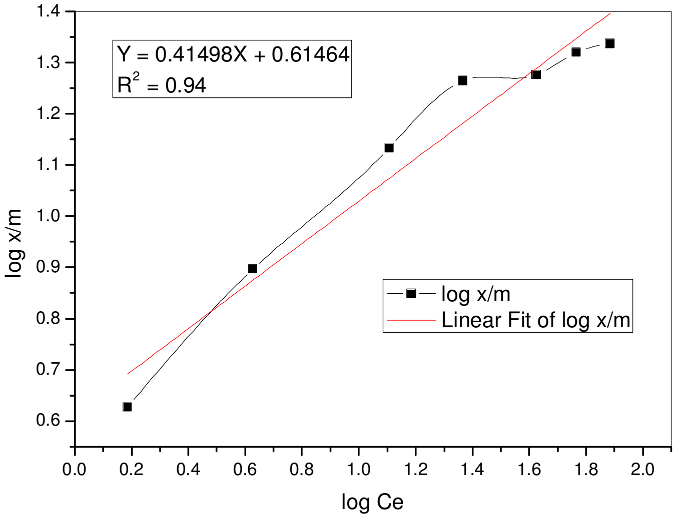

Fig. 5 (d). Freundlich plot of fluoride adsorption on type-II sand.

IV. CONCLUSION AND FUTURE PERSPECTIVES

The present study investigated the potential of native sand materials for adsorption of fluoride as a function of pH, adsorbent dose, fluoride concentration and contact time. Under optimized conditions of pH-5.5, adsorbent dose-20 g/L, with fluoride concentration-10 mg/L for contact time-2 hrs, the maximum 80.3 and 84.7 % fluoride removal was observed with both type-I and type-II sand materials. The adsorption data obtained with both adsorbents were fitted to both Langmuir and Freundlich isotherms but was better correlated to Langmuir model.

The experimental findings suggested that the locally available low cost sand material which is available in abundance are found to exhibit a good fluoride adsorption capacity under optimized conditions and can be used to develop community based low cost technology for defluoridation of water as a solution where no other source of clean and potable drinking water is available.

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