



## Applicability assessment of LECA and $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA for removing nitrate from drinking water

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### ABSTRACT

In this study we investigated the potential of lightweight expanded clay aggregate (LECA), a material used in the construction industry, and its doped form ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA), as new adsorbents for nitrate treatment in drinking water. Their characteristics were analysed, including morphology *via* scanning electron microscopy, particle zeta potential through the dynamic light scattering method, and field emission scanning electron microscopy. To elucidate the mechanisms and potential of nitrate removal, and optimize the influential factors, we considered the initial nitrate concentration 100, 200 mg/L, adsorbent dose 10, 20, 30, 50, and 70 g/L, contact time 0.5, 1, 3, and 5 h, and aqueous pH levels ~2, ~4.5, and ~7. The results showed that maximum nitrate adsorption was approximately 35% after a contact time of 0.5 h in a solution containing 10 g/L LECA and an initial nitrate concentration of 100 mg/L. However, this process rapidly diminished with the continuation of the contact time, proving a “desorption phenomenon” occurring in the solution. In the case of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA, the maximum adsorption was around 65% at the contact time up to 1.75 h, but a similar trend was observed. Overall, since the desorption of nitrate ions occurs rapidly and is not desirable for practical use, further research on these adsorbents may clarify their practical efficiencies in treating other non-desirable substances.

**Keywords:** Nitrate treatment; Adsorption; Lightweight expanded clay aggregate (LECA);  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA; Batch test

### 1. Introduction

Nitrate is highly water-soluble, and can easily transfer into the rivers and lakes, or leach through the subsoil into the groundwater aquifers. Generally, nitrate is present in the fertilizer used on agricultural farms, in sewage from sheep and cattle barns, and effluent from factories. High levels of nitrate in drinking water can cause health and environmental problems such as methemoglobinemia, (which leads to blue-baby syndrome), impairing the immune system, and stress in certain aquatic species. While

in many parts of the world, especially remote area and villages in developing countries, groundwater supply is the only source of drinking water, the issue of excess nitrate in water has become an important environmental quality and health concern. Reported nitrate concentration in groundwater of 10 provinces in Iran, which their data have been available is presented by Zندهbad et al. [1]. According to this article, in all cases the maximum nitrate concentration is about 200 mg/L and in one of the case a figure of 428 mg/L is reported.

The Environmental Protection Agency (EPA) has set the maximum contaminant level for nitrate in drinking

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water at up to 50 mg/L  $\text{NO}_3^-$  [2]. Hence, reducing or omitting the nitrate from groundwater has become a great concern for the local water supply authorities. This issue has prompted authorities and researchers to develop techniques to address the problem and reduce or remove nitrate from drinking water. The methods and techniques employed include chemical precipitation [3], distillation, reverse-osmosis [4], electro dialysis [5], ion exchange [6–9], bio-denitrification [10–15] and adsorption [16–24]. Most of these have some restrictions, such as the high installation cost, low efficiency, and requirement of post-treatment. However, approaches based on the adsorption technique reduce the limitations and offer advantages such as lower cost, ease of implementation, and adaptability to variable environmental conditions. Common adsorbents used in this technique are a group of carbon-based materials such as natural agricultural and industrial wastes, as well as bio-sorbents. Additionally, chemically treated materials, including zinc chloride-treated granular activated carbon [24], iron oxide-dispersed activated carbon fibers [25], and commercial activated carbon [26] are also utilized. In this context, the research aimed at developing a medium with a higher reaction rate has been ongoing for some time. Most researcher's efforts have been focused on finding adsorbents with higher efficiency and lower cost.

The use of nanomaterial for nitrate removal from drinking water is also reported by Bekhradinassab and Sabbaghi [18]. In this study, they utilized nano- $\text{SiO}_2\text{-FeOOH-Fe}$  and achieved the removal of 99.84% of nitrate from drinking water under optimal conditions.

Natural clays are a significant and practical sorbents due to their low-cost, availability, and easy applications in removal of the environmental contaminants. Various clays and clay minerals play a crucial role in the environment and were used as effective adsorbent materials for the ions removal from water solutions [27]. These minerals are, abundant, cheap, locally available, and effective adsorbent materials which have been successfully used as adsorbents for certain elements and metals in aqueous solutions. Clays, in both in their natural and modified forms, are effective at removing a variety of heavy metals from water. One of the reasons for their effectiveness is that they contain exchangeable cations and anions attached to their surface. This has led scientists worldwide to focus on using natural or modified clay materials as adsorbents for water treatment. Clay minerals have interlayer spaces, which is why they can adsorb toxic metals present in water. Most of the clays can swell, increasing the space between their layers to accommodate the adsorbed water and ionic species

[27]. Montmorillonite and vermiculite are particularly noteworthy due to their large specific surface area and high cation exchange capacity [28]. As a result, clay minerals are important sorbent, which significantly contribute to the sorption of a range of polar and aromatic compounds.

In the construction industry, a kind of lightweight expanded clay aggregate (LECA) is produced which consists of small, lightweight, bloated particles of burnt clay with high porosity [29]. Fig. 1 represents LECA particles in different size. This product is universally accessible and is entirely natural at a low-cost. LECA is environment-friendly with no dangerous leaching, even when in contact with soil, water, or rain [30].

Characterization, isotherm, and kinetic studies for ammonium ion adsorption by LECA is reported by Sharifnia et al. [29]. They stated that LECA can be used for ammonium ion removal as a low-cost and green sorbent. LECA has been used as an adsorbent for the removal of some toxic materials and metals by Abollino et al. [28]. The removal of heavy metals from the paint industry's wastewater using LECA as an available adsorbent was investigated by Malakootian et al. [31]. According to the results presented, LECA is recommended as a low-cost and available adsorbent to remove lead and cadmium from wastewater generated in the paint industry. Studies have been also conducted on water defluoridation using LECA [32]. They reported that fluoride removal efficiency increases with the initial fluoride concentration, adsorbent mass, and reaction time, but decreased with pH and ionic strength increases. The efficiency of powdered LECA for the treatment of nitrate in dairy wastewater, in the presence of other impurities, have been investigated by Dharani et al. [33]. They reported a 63% removal capacity for nitrate at a mixing speed of 200 rpm and 4 g/L of adsorbent dose. However, they reported that this happened after 30 min and diminished afterward.

The LECA aggregates surface can be chemically modified to enhance its capacity to remove impurities from water. The use of Fenton-modified LECA as an adsorbent for arsenite and arsenate removal from aqueous solutions has been documented by Amirri et al. [34]. The adsorptive removal capacity of tetracycline (TC) from an aqueous solution by LECA manganese oxide nanoparticle-coated LECA in the presence of hydrogen peroxide was also evaluated [35]. Under optimal conditions, the maximum TC removal percentage were reported to be 51.5% for LECA and 99.4% for manganese oxide nanoparticle-coated LECA. The application of LECA, enhanced with a coating to improve its adsorption capacity, for nitrate removal from water has been documented by Stefaniuk et al. [36] and Fu et al. [37]. These studies reported the use of nano-zero-valent iron (nZVI) for removing or decreasing nitrate from water. However, the application of nZVI as a coating substance has its drawbacks. These include instability, challenges in separating it from the medium being purified, rapid passivation of the material, and limited particle mobility due to agglomeration, as reported also in other various studies [36–39]. To confront the negative points accompanying the use of nZVI, various modifications have been made as suggested by Mueller et al. [38], these include the admixtures of other metals to nZVI, the emulsification of nZVI, the deposition of nZVI on a carrier,



Fig. 1. Various sizes of LECA particles [30].

or trapping of nZVI in a matrix. Furthermore, studies also have been undertaken, aimed at innovation of the techniques of production, physicochemical functionality, and enhanced stability and mobility of those particles [40]. One of the methods of stabilizing metals is to make them into an oxide form and fix it on the material [40]. Synthesis of materials covered by Iron oxide is reported by Rasouli et al. [41] and Ulfa et al. [42]. Based on the researches,  $\text{Fe}_2\text{O}_3$  (hematite) has three basic phases:  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\beta\text{-Fe}_2\text{O}_3$ , and  $\gamma\text{-Fe}_2\text{O}_3$ . Among these,  $\alpha\text{-Fe}_2\text{O}_3$  is the most stable and environment friendly iron oxide. This oxide's stability is attributed to the strong interaction among the electrons, which exhibits chemical stability over a broad pH range, making it suitable for photocatalytic applications. Removal of nitrate from aqueous solution using zerovalent iron-reduced graphene oxide composite evaluated by Khoshro et al. [39]. They reported that nitrate-contaminated water can be easily treated by applying the synthesized composite within the short contact time of 1 min. Irrespective of these, limited studies has been reported for application of LECA and  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ , as a clay-based material, in nitrate removal from water. This study is designed to evaluate the potential of LECA and  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  as adsorbents in the removal of nitrate ions from drinking water while considering their characteristics and the effect of contact time, initial nitrate concentration, dosage of the LECA and the pH of the solution on their performance.

## 2. Material and methods

In this study, batch tests were implemented to evaluate the effect of different variables on the adsorption of nitrate by readily available LECA and synthesized coated LECA as  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

### 2.1. LECA preparation

A pack of LECA with an aggregate size ranging from 2 to 4 mm, was acquired from a producing company in Tehran, Iran. Initially, the entire contents of the pack were immersed in distilled water for several days and rinsed multiple times to eliminate impurities, dust, and undesirable components. Following this, it was dried in an oven at 120°C until the weight became constant. The prepared material pack was then stored in a clean and dry storage to be ready for experiments and characteristic determination.

### 2.2. Chemicals and lab equipment

Potassium nitrate ( $\text{KNO}_3$ , E. Merck KG, Darmstadt, Germany, 98%) was used to prepare a stock solution of 1,000 ppm concentration of nitrate ion in deionized water. A specific volume of the stock solution was further diluted with deionized water to achieve the required concentrations for different tests. The pH and electrical conductivity of the solutions were measured using a portable pH and conductivity meter (Hach HQ40D Meter, Made by HACH Company American Production). Prior to performing the tests, electrical conductivity of the solutions were measured to be in the range of 300–400  $\mu\text{S}/\text{cm}$  and their pH were in the neutral  $\sim 7$  level. Hydrochloric acid (HCl)

and acetic acid ( $\text{CH}_3\text{COOH}$ ) (E. Merck KG, Darmstadt, Germany) were also used for preparing different pH levels in the conducted tests. Nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , E. Merck KG, Darmstadt, Germany) was utilized to coat  $\text{Fe}_2\text{O}_3$  on LECA aggregates, producing  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

The concentration of nitrate in the test solutions was measured using the Ion Chromatography Method, utilizing the 930 Compact IC equipment from Metrohm Company, Switzerland. The samples morphology and elemental composition were analysed using scanning electron microscopy (TESCAN VEGA3, Czech Republic). Zeta potential of LECA and  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  was determined using the HORIBA DLS Version SZ100 instrument (Horiba Ltd., Japanese).

The  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  was produced using a variety of equipment including a digital weigh indicator (AND/GR-200), an orbital shaker (SLTS-100, Canada), an oven (U30, Netherlands), a centrifuge machine (Hetich/Universal 320, Germany), tube furnaces (TFM5/40 1200, Iran), and an ultrasonic bath (XB2, England). The structure of the LECA particles was examined using scanning electron microscopy (SEM). The zeta potential of the particles was measured by dynamic light scattering (DLS) technique. Furthermore, to get a more detailed view of the  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ 's structure, field emission scanning electron microscopy (FESEM) was employed due to its superior resolution. The particle images were further magnified using a binocular microscope.

### 2.3. $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ synthesis

The synthesis of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  was carried out according to the method outlined by Rasouli et al. [41]. This method utilizes an ultrasound-assisted pathway and a wet impregnation technique. In this process, LECA is mixed with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  dissolved in ethanol, resulting in the formation of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

In the laboratory, LECA was immersed in ethanol and agitated with a magnetic stirrer for a duration of 5 min. Following this,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added to the solution and gently mixed for 1 h at a temperature of 25°C and atmospheric pressure. The mixture was then sonicated for 8 min. Subsequently, the ethanol was evaporated overnight at 115°C. The final step involved preparing  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  by annealing the product at approximately 400°C for 3 h, then after, it was washed with ethanol and dried at 90°C for 2 h.

### 2.4. Batch tests setup for LECA

In this research, several series of batch tests were conducted to assess the effect of various factors on the adsorption of nitrate by LECA. The variables examined included the initial nitrate concentration 100 and 200 mg/L, LECA adsorbent dosage in the solution 10, 20, 30, 50, and 70 g/L, and contact time 0.5, 1, 3, and 5 h. These tests were repeated under three different pH conditions:

- Initial solution pH ( $\sim 7$ ), denoted as  $T_1$  condition;
- pH was reduced, adding a few drops of hydrochloric acid (pH  $\sim 2$ ), denoted as  $T_2$  condition, and
- pH was reduced by addition of acetic acid (pH  $\sim 4.5\text{--}5$ ), denoted as  $T_3$  condition.

The tests were conducted in such a manner that for each test, the initial nitrate concentration, adsorbent (LECA) dosage, and the pH were held constant, while varying the contact time. At the end of the designated contact time, a sample of the solution was taken and filtered using JIAO JIE102 filter paper. The nitrate concentration was then determined using the ion chromatography method. Throughout all test series, the flask containing the solution was stirred at a speed of 100 rpm for the specified contact time using a stirrer shaker. The removal efficiency,  $R$ , was calculated using Eq. (1), which considers the difference between the initial solution concentration ( $C_0$  in mg/L) and the final reading ( $C_i$  in mg/L). Additionally, the net amount of nitrate adsorbed per unit mass of adsorbent,  $q$  (mg/g), was determined at the end of the contact time using Eq. (2).

$$R = \frac{C_0 - C_i}{C_0} \quad (1)$$

$$q = \frac{C_0 - C_i}{L} \quad (2)$$

where  $L$  is the adsorbent dose (g/L).

### 2.5. Batch test setup for $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA

The insights and results obtained from the LECA tests were instrumental in designing more efficient batch tests for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA with fewer iterations. The number of tests and the range of variables, as mentioned in the LECA tests, were determined based on the output from the Design-Expert software [43]. This software offers robust tools to design an optimal experiment for the process, mixture, or combination of factors and components. As per the suggested layout, the variables taken into account included: initial nitrate concentrations of 50, 100, 150, and 200 mg/L; adsorbent dosage of 10, 25, 40, 55, and 70 g/L; contact times of 0.5, 1.75, 3, 4.25, and 5.5 h, and a pH range of 2, 4, 6, 8, and 10.

For this test series, all laboratory procedures, analytical methods, and subsequent calculations are conducted in a manner similar to the LECA tests.

### 2.6. Adsorption isotherm study

Commonly, the Langmuir [Eq. (3)] and Freundlich [Eq. (4)] models are utilized to estimate the equilibrium concentration and the quantity of solute adsorbed in the aqueous phase [44].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

where  $q_m$  is maximum adsorption capacity (mg/g),  $K_L$  is sorption equilibrium constant (L/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L) and  $q_e$  is the amount adsorbed at equilibrium (mg/g). In Eq. (4),  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity

and adsorption intensity. The value of  $K_F$  and  $n$  are derived from the intercept and slope of the plots of  $\log q_e$  vs.  $\log C_e$ . Generally, higher values of  $n$  and  $K_F$  indicate a greater adsorption capacity of the adsorbent at equilibrium phase. Furthermore, the linearized Langmuir isotherm derived from Eq. (3) is presented by Eq. (5). To evaluate the adsorption efficiency in equilibrium, the dimensionless equilibrium parameter ( $r$ ) is computed using Eq. (6), with values  $< 1$  indicating auspicious adsorption.

$$\frac{C_e}{q_e} = \left[ \frac{1}{K_L q_m} \right] + \left[ \frac{1}{q_m} \right] C_e \quad (5)$$

$$r = \frac{1}{1 + K_L C_0} \quad (6)$$

## 3. Results and discussion

### 3.1. LECA and $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA characterization

The SEM image of LECA depicted in Fig. 2a reveals the morphology of the particles, which consist of a porous structure with embedded pores. This configuration results in high porosity and a specific surface area for the particles, suggesting that LECA particles could be an effective adsorbent. Moreover, the surface condition of the particle is conducive to doping the particles with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The FESEM images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA are shown in Fig. 3. These images indicate that the LECA voids are filled producing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA. A magnified image from the binocular microscope, presented in Fig. 2b, further demonstrates that both the pores and the surface of the particles are thoroughly coated with Fe<sub>2</sub>O<sub>3</sub> during the synthesis process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA.

Energy-dispersive X-ray (EDX) microanalysis is a method of elemental analysis that is used in conjunction with electron microscopy. It operates on the principle of generating characteristic X-rays, which can identify the presence of various elements within the specimens. The EDX analysis and elemental mapping of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA, along with the FESEM, are displayed in Fig. 4. The data from the EDX analysis indicates that the doped particles contain 24.11% of iron (Fe) by weight. The weight percentages of other elements are also depicted in Fig. 4.

The zeta potential of the LECA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA particles, as measured by DLS, are depicted in Fig. 5a and b, respectively. The zeta potential is a measure of the electrical charge at the surface of the hydrodynamic shear that surrounds colloidal particles. It plays a crucial role in determining the long-term stability and physical properties of any particle in suspension. Typically, a zeta potential value of either +30 or -30 mV is considered the threshold between stable and unstable suspensions [45]. Particles with zeta potentials greater than +30 mV or less than -30 mV are generally deemed stable. However, if the particles have a density higher than the dispersant, they will eventually precipitate and form a close-packed bed (i.e., a hard cake), even if they are initially dispersed. The zeta potential for LECA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@LECA are approximately -34 and -25 mV,

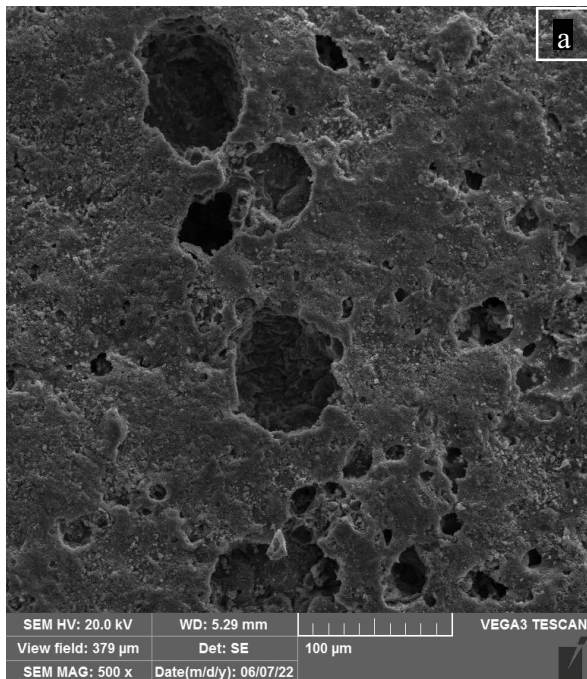


Fig. 2. (a) Scanning electron microscopy image of LECA particles and (b) binocular microscope image of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

respectively (as shown in Fig. 5). This suggests that LECA is in a stable condition, while  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  is relatively stable.

### 3.2. Tests performance

The results from the tests conducted on the LECA and the  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  are presented.

#### 3.2.1. LECA tests

The results of the tests conducted on LECA are tabulated in Table 1 for neutral pH condition ( $T_1$  condition), Table 2 for  $T_2$  and Table 3 for  $T_3$  pH conditions. These tables show the final nitrate concentration after 0.5 h contact (stirring)

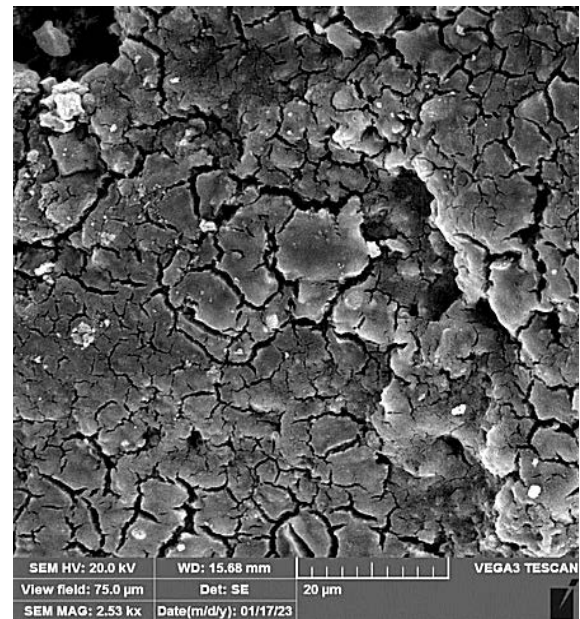


Fig. 3. Field emission scanning electron microscopy image of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

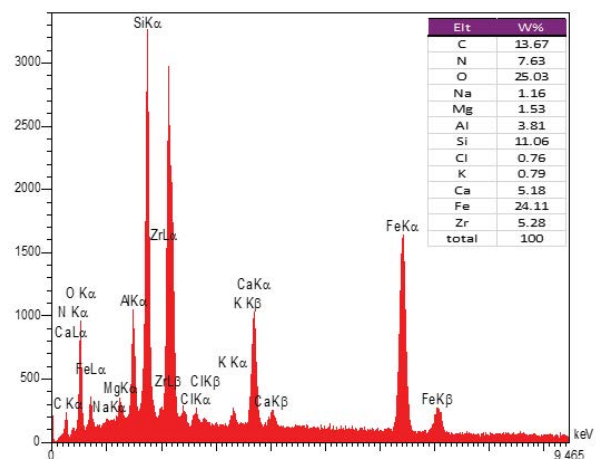


Fig. 4. Field emission scanning electron micrograph along with energy-dispersive X-ray analysis and elemental mapping of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

time and for different LECA dosage while different initial nitrate concentrations (100 and 200 mg/L) were utilized. In the tables, column: 'ID' is the test number, ' $C_0$ ' is the initial nitrate concentration, ' $t$ ' is the contact times, ' $L$ ' is the adsorbent (LECA) dosage, ' $C_t$ ' is the nitrate concentration measured at the end of the ' $t$ ' time, ' $R\%$ ' is the removal efficiency, and ' $q$ ' is the nitrate reduction mass per unit mass of LECA dosage (designated as 'net removal'). The results of other contact periods have not been included here due to their length. Also, to check the performance of the very low LECA dosage (<10 g/L), several supplementary and repeated experiments were conducted on the dosage of 2, 3, and 5 g/L. The results showed inconsistent and uncoordinated  $R$  and  $q$  (in some cases negative values) in relation

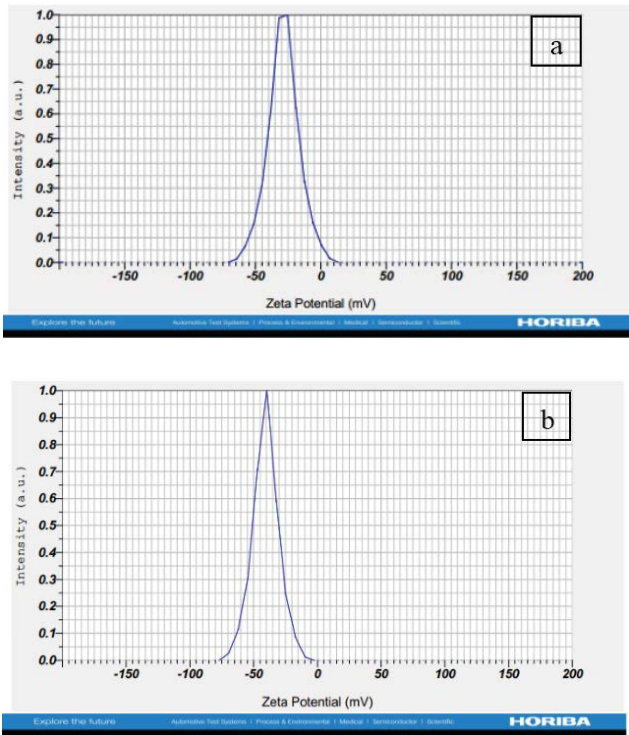


Fig. 5. Graph of zeta potential, (a) LECA particles and (b)  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

Table 1  
Removal efficiency ( $R$ ) and net removal ( $q$ ) for varying adsorbent and initial nitrate concentration in  $T_1$  condition

ID	$C_0$ (mg/L)	$t$ (h)	$L$ (g/L)	$C_i$ (mg/L)	$C_0 - C_i$ (mg/L)	$R$ (%)	$q$ (mg/g)
$C_1T_1L_1$	100	0.5	10	65.2	34.8	34.8	3.48
$C_1T_1L_2$	100	0.5	20	95.9	4.1	4.1	0.21
$C_1T_1L_3$	100	0.5	30	92.3	7.7	7.7	0.26
$C_1T_1L_4$	100	0.5	50	93.9	6.1	6.1	0.12
$C_1T_1L_5$	100	0.5	70	91.2	8.8	8.8	0.13
$C_2T_1L_1$	200	0.5	10	128.3	71.6	35.8	7.16
$C_2T_1L_2$	200	0.5	20	176	24	12	1.2
$C_2T_1L_3$	200	0.5	30	183	17	8.5	0.57
$C_2T_1L_4$	200	0.5	50	180.4	19.6	9.8	0.39
$C_2T_1L_5$	200	0.5	70	184	16	8	0.23

to the LECA dosages and the initial concentrations (not presented here). In following the effects of pH, initial nitrate concentration, adsorbent dosage, and contact time in reducing the nitrate concentration are examined.

### 3.2.1.1. Effect of pH

In general, the adsorption of nitrate can vary under different pH conditions. This variation is influenced by the properties of the adsorbent material and the chemistry of the solution [46]. Typically, adsorbents possess positive surface

Table 2  
Removal efficiency ( $R$ ) and net removal ( $q$ ) for varying adsorbent and initial nitrate concentration in  $T_2$  condition

ID	$C_0$ (mg/L)	$t$ (h)	$L$ (g/L)	$C_i$ (mg/L)	$C_0 - C_i$ (mg/L)	$R$ (%)	$q$ (mg/g)
$C_1T_1L_1$	100	0.5	10	157.9	—*	—*	—*
$C_1T_1L_2$	100	0.5	20	204	—	—	—
$C_1T_1L_3$	100	0.5	30	166.5	—	—	—
$C_1T_1L_4$	100	0.5	50	277.6	—	—	—
$C_1T_1L_5$	100	0.5	70	253.1	—	—	—
$C_2T_1L_1$	200	0.5	10	365.9	—	—	—
$C_2T_1L_2$	200	0.5	20	287.7	—	—	—
$C_2T_1L_3$	200	0.5	30	401.7	—	—	—
$C_2T_1L_4$	200	0.5	50	416.1	—	—	—
$C_2T_1L_5$	200	0.5	70	472.3	—	—	—

\*These figures are not presented as they are invalid.

Table 3  
Removal efficiency ( $R$ ) and net removal ( $q$ ) for varying adsorbent and initial nitrate concentration in  $T_3$  condition

ID	$C_0$ (mg/L)	$t$ (h)	$L$ (g/L)	$C_i$ (mg/L)	$C_0 - C_i$ (mg/L)	$R$ (%)	$q$ (mg/g)
$C_1T_1L_1$	100	0.5	10	72.6	27.4	27.4	2.74
$C_1T_1L_2$	100	0.5	20	93	7	7	0.35
$C_1T_1L_3$	100	0.5	30	96	4	4	0.13
$C_1T_1L_4$	100	0.5	50	95.5	4.5	4.5	0.09
$C_1T_1L_5$	100	0.5	70	97.5	2.5	2.5	0.04
$C_2T_1L_1$	200	0.5	10	131.4	68.5	34.2	6.85
$C_2T_1L_2$	200	0.5	20	169.8	30.1	15.1	1.51
$C_2T_1L_3$	200	0.5	30	178.9	21	10.5	0.7
$C_2T_1L_4$	200	0.5	50	184.1	15.8	7.9	0.32
$C_2T_1L_5$	200	0.5	70	190.9	9.1	4.5	0.13

charges at lower pH values, which promote the binding of negatively charged nitrate ions through electrostatic interactions. However, when the pH value is extremely low (below 2), hydrogen ions may compete with nitrate ions for binding sites on the adsorbent surface, leading to a decrease in nitrate adsorption. At a neutral pH (around 7), some adsorbents may have a zero net surface charge or even a slightly negative charge. Nitrate adsorption within this range can be affected by other elements, such as the competition from other anions or co-adsorption with cations. The adsorption of nitrate may decrease due to the presence of other competing anions, given their similar affinity for the binding sites on the adsorbent [47]. Numerous studies have indicated that nitrate adsorption is generally higher under acidic pH conditions as compared to basic conditions [47–51]. In this study, we observed that the zeta potential of the LECA is negative, which is not conducive to the adsorption of negative nitrate anions. Therefore, we decided to conduct the tests under acidic pH conditions to enhance the affinity potential for nitrate adsorption. The results obtained from these tests are

discussed in the subsequent sections. The test results under  $T_1$  condition (pH  $\sim 7$ ), as shown in Table 1, generally, indicate a decrease in the final nitrate concentration. This suggests that LECA has adsorption capacity even at neutral acidity. Given that the initial nitrate source was pure analytical potassium nitrate ( $KNO_3$ ) added to deionized water, and there were virtually no other competing anions in the solution, any observed adsorption potential can be solely attributed to the characteristics of the LECA particles. Conversely, the results from the  $T_2$  condition tests, where the pH of the solution was reduced to approximately 2 by adding HCl (Table 2), unexpectedly show that the final nitrate concentrations were inconsistent and significantly higher compared to the initial concentrations. This discrepancy could potentially be due to a chemical reaction between the strong HCl acid and the LECA particles, which may have partially dissolved the LECA materials. Observations showed that in contrast to the  $T_1$  condition, which the electrical conductivity of the solutions remained relatively constant during the stirring time, the  $T_2$  condition showed a significant increase in electrical conductivity of the final solutions. It rose from approximately 350  $\mu S/cm$  to about 11,000  $\mu S/cm$  by the end of the tests. This increase provides evidence of a chemical reaction between the LECA particles and the HCl acid. As the result, we concluded that using a strong acid to lower the pH of the solution is not appropriate and the final concentrations are not valid. Therefore, a weaker acid was used to drop down the pH level and in the  $T_3$  condition, we used acetic acid to reduce the pH of the solutions to approximately 4.5 level. The results of these tests, shown in Table 3, indicate a decrease in the final nitrate concentration, suggesting that the LECA particles have adsorbed the nitrate from the solution. However, when comparing the results of  $T_3$  with those of  $T_1$ , it appears that while nitrate adsorption also occurred under  $T_3$  condition, the nitrate removal capacity of LECA at neutral acidity ( $T_1$ ) was slightly higher. This is surprising as we expected higher adsorption at the lower pH of  $T_3$  condition. The observed decrease in adsorption at lower acidity pH levels could potentially be due to competition between hydroxide ions and nitrate ions. However, this observation seems to contradict the findings of a previous study [48], which investigated a different type of local clay with a structure distinct from LECA. This suggests that the adsorption capacity of adsorbents is not solely determined by pH, but also by their unique composition, even though both are clay-based materials.

### 3.2.1.2. Effect of LECA dosage

Upon examining the final nitrate concentration in relation to the LECA dosage as shown in Tables 1 and 3, it is observed that although the final concentrations decreased across all LECA dosages, net removal was lower for higher LECA dosages. As a result, both the removal efficiency ( $R$ ) and net removal ( $q$ ) decreased. For a dosage of 10 g/L, the  $R$  value is approximately 35%, which is the maximum under  $T_1$  condition (Table 1) for both initial nitrate concentrations, and it decreases for higher dosages. In the  $T_3$  condition (Table 3), the  $R$  values are 27.4% for a 100 mg/L nitrate solution and 34.2% for a 200 mg/L nitrate solution, and they decrease with higher dosages, similar to the  $T_1$  condition.

The plots of ( $R$ ) and ( $q$ ) vs. LECA dosage shown in Fig. 6a for  $T_1$  and 6b for  $T_3$  conditions reveal a significant drop in efficiency and net removal, which remains nearly constant for dosages greater than 20 mg/L. These observations contradict the findings by Battas et al. [48], which indicated a positive correlation between the dosage of clay and the  $R$  value. Interestingly, they reported a maximum  $R$  value of 35% for 40 g/L of local clay, tested with a 100 mg/L nitrate solution in distilled water. In the present study, the maximum  $R$  value is also 35%, but it's achieved with a 100 mg/L nitrate solution and a 10 g/L LECA dosage. It's important to note that both the adsorbent and the nitrate solution used in this study differ from those by Battas et al. [48]. Here, the nitrate solution is prepared in deionized water and the adsorbent is LECA aggregates which are basically clay materials, but they are blotted and disfigured by heat.

### 3.2.1.3. Effect of initial nitrate concentration on nitrate removal

The initial nitrate concentrations, when higher (200 mg/L), resulted in greater nitrate removal as indicated by the  $q$  values. This suggests that a specific dose of

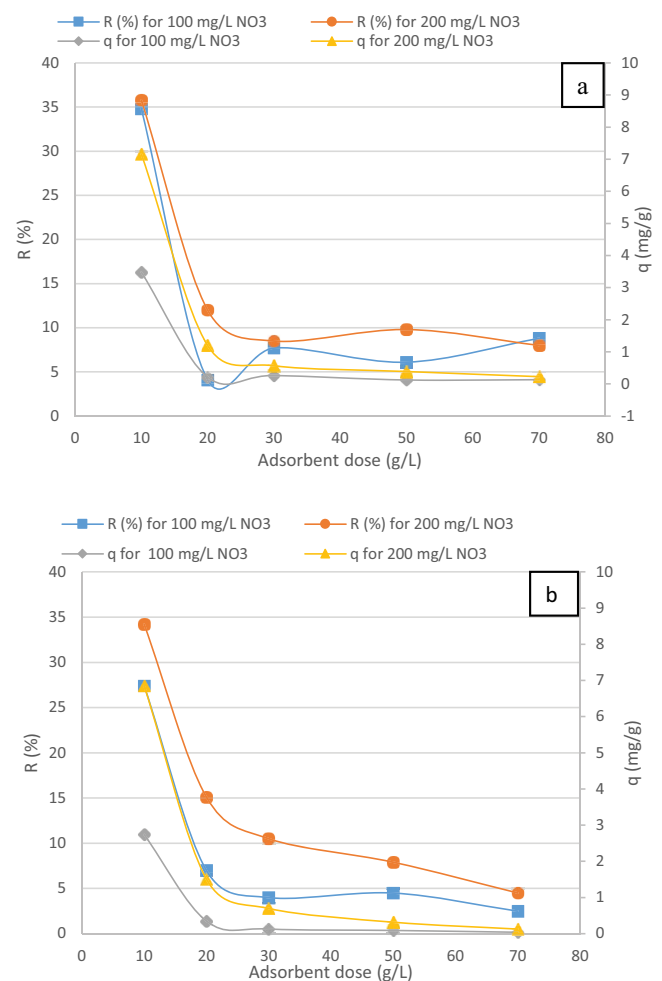


Fig. 6. Effect of LECA dosage on removal efficiency ( $R$ ) and the net removal ( $q$ ) of nitrate at different initial nitrate concentrations (a) under  $T_1$  conditions and (b) under  $T_3$  conditions.

LECA has the capacity to adsorb more nitrate when the initial concentrations are higher. However, this effect was observed alongside a decrease in  $R$  values as the LECA dose increased. A closer look at the results under  $T_1$  condition, as shown in Table 1, reveals that with a LECA dose of 10 g/L, the net mass of nitrate removed, denoted as  $q$ , is 3.5 mg/g in a solution with an initial nitrate concentration of 100 mg/L, and 7.1 mg/g in a solution with an initial concentration of 200 mg/L. In general, the  $q$  value is consistently higher for the 200 mg/L concentration compared to the 100 mg/L concentration across all LECA dosage cases. This outcome suggests that when the initial nitrate concentration is higher, a specific dose of LECA aggregate is capable of adsorbing more nitrate from the solution. However, contrary to expectations, we noticed that the  $q$  value decreases with an increase in the LECA dose in both nitrate solutions, mirroring the trend observed in the  $R$  values. The results under  $T_3$  condition, as detailed in Table 3, exhibit similar patterns to those explained for  $T_1$  condition. The relationship between  $q$  and LECA dosage for both condition is depicted in Fig. 6a and b. The observed contradiction in the expected outcomes for  $R$  and  $q$  values implies that either desorption phenomena or the low concentration of the initial solution could be potential factors contributing to this occurrence. In our experiment, we do not consider the second reason to be plausible, as the same observation is made even at a concentration of 200 mg/L. However, it's more likely that desorption occurs in the presence of a higher dosage of the adsorbent.

3.2.1.4. Effect of contact time

Table 4 presents the results of the removal efficiency ( $R$ ) and the net nitrate removal ( $q$ ) from various initial concentrations under  $T_1$  and  $T_3$  conditions. This was observed in the presence of a 10 g/L LECA dose over different contact times. The nitrate removal efficiency ( $R$ ) for LECA was highest within the first 30 min of contact time and gradually decreased, reaching equilibrium at less than 10% in about 1 h. This pattern suggests that desorption occurs over time. Fig. 7a presents a plot of the ( $R$ ) and ( $q$ ) values against the contact time under  $T_1$  condition. As depicted

in this figure, the  $R$  values for both initial concentrations reach as high as 35% within the first 30 min, then gradually approach equilibrium at less than 10% in about 1 h.

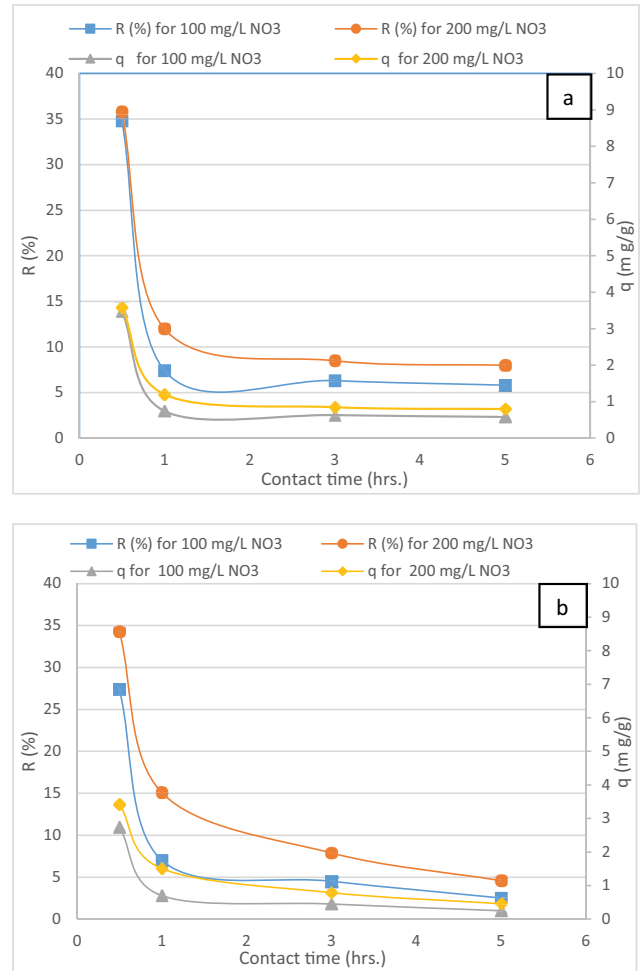


Fig. 7. Effect of contact time on the removal efficiency ( $R$ ) and the net removal ( $q$ ) at different initial nitrate concentration using 10 g/L LECA in (a)  $T_1$  and (b)  $T_3$  conditions.

Table 4

Removal efficiency ( $R$ ) and the net removal ( $q$ ) of LECA in different contact periods for 10 g/L LECA dosage and for  $T_1$  and  $T_3$  conditions

ID	$t$	$L$	$T_1$ condition			$T_3$ condition			
			$C_0$	$C_i$	$R$	$q$	$C_i$	$R$	$q$
			(mg/L)	(mg/L)	(%)	(mg/g)	(mg/L)	(%)	(mg/g)
$C_1T_1L_1$	0.5	10	65.2	34.8	3.48	72.6	27.4	2.74	
$C_1T_2L_1$	1	10	92.6	7.4	0.74	93	7	0.7	
$C_1T_3L_1$	3	10	93.7	6.3	0.63	95.5	4.5	0.45	
$C_1T_4L_1$	5	10	94.2	5.8	0.58	97.5	2.5	0.25	
$C_2T_1L_1$	0.5	10	164.2	35.8	3.58	165.7	34.3	3.43	
$C_2T_2L_1$	1	10	188	12	1.2	184.9	15.1	1.51	
$C_2T_3L_1$	3	10	191.5	8.5	0.85	192.1	7.9	0.79	
$C_2T_4L_1$	5	10	192	8	0.8	195.4	4.6	0.46	



Considering the net removal for both nitrate concentrations, the  $q$  values reach as high as 3.5 mg/g, and then settle to less than 1 mg/g within an hour. In the case of  $T_3$  condition, as shown in Fig. 7b, the ( $R$ ) and ( $q$ ) values follow a similar trend, achieving equilibrium after 1 h. As the contact time extends, nitrate ions are released and desorption occurs. These findings suggest that LECA aggregate may not be suitable for practical nitrate removal from water in industrial applications. A similar observation was reported by Battas et al. [48], where desorption began after 2 h when using a local clay material. The authors suggest that the discharge of nitrate ions could be attributed to the saturation of unoccupied adsorption sites on clay particles. They also propose, in line with Freundlich's hypothesis that the binding energy diminishes exponentially as surface saturation increases [44]. Moreover, in this study, it's likely that the negatively charged LECA aggregates (with a zeta potential of  $-34$  mV) repel the similarly charged nitrate anions, releasing them after a brief contact period. However, LECA could be an appropriate material for positively charged cations like ammonium, as indicated in previous research [29].

### 3.3. Results of the batch tests for $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$

Table 5 shows the results of both the removal efficiency ( $R$ ), and the net removal ( $q$ ), for the batch tests conducted on  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . These results were obtained by applying the range of variables suggested by the Design-Expert software [43]. In these tests, LECA particles act as the carrier for the hematite ( $\text{Fe}_2\text{O}_3$ ) and any removal of nitrate

Table 5  
Removal efficiency ( $R$ ) and the net removal ( $q$ ) of nitrate in relation to varying dosage of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ , initial nitrate concentration, contact time, and pH level

Number	$L$ (g/L)	pH	$C_0$ (mg/L)	$C_i$ (mg/L)	$t$ (h)	$R$ (%)	$q$ (mg/g)
1	40	6	50	34.75	3	30.5	0.38
2	55	4	100	46	4.25	54	0.98
3	55	8	100	50	4.25	50	0.91
4	25	8	100	36.7	4.25	63.3	2.53
5	25	4	100	40	1.75	60	2.40
6	25	4	100	45.5	4.25	54.5	2.18
7	55	4	100	42.6	1.75	57.4	1.04
8	55	8	100	37.8	1.75	62.2	1.13
9	25	8	100	34.1	1.75	65.9	2.64
10	10	6	150	130.95	3	12.7	1.91
11	70	6	150	138.15	3	7.9	0.17
12	40	6	150	115.35	0.5	23.1	0.87
13	40	6	150	125.4	5.5	16.4	0.62
14	40	10	150	139.05	3	7.3	0.27
15	40	6	150	133.5	3	11.1	0.41
16	40	2	150	126.45	3	15.7	0.59
17	55	8	200	196.8	1.75	1.6	0.06
18	25	8	200	192.4	1.75	3.8	0.30

is attributed to the presence of this oxide apart from the adsorption capacity exclusive to the particles. Assuming that both capacities are in effect, we would anticipate a higher nitrate removal capacity compared to the LECA tests. However, this comparison is only valid if a comparable range of parameters is applied.

The results of these tests reveal that in a solution with an initial nitrate concentration of 100 mg/L at pH 8, the maximum  $R$  value is 65%, and  $q$  equals 2.64 mg/g. This suggests that a basic pH promotes nitrate adsorption by  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ , unlike the results from the LECA tests. In the LECA experiment, the maximum  $R$  value is 35% with a 100 mg/L nitrate solution and 10 g/L adsorbent in neutral and acidic pH conditions. Generally, for all tests with an initial nitrate concentration of 100 mg/L, the  $R$  and  $q$  values are higher compared to other concentrations. This likely indicates the limited adsorption capacity of aggregates at higher concentrations. At pH 8, the  $R$  and  $q$  values increase for all three initial nitrate concentrations. However, in the LECA tests, nitrate removal is more efficient under neutral and mildly acidic pH conditions. For all three initial concentrations, the majority of nitrate removal occurs in the early stages of contact time, with the  $R$ -value decreasing as time progresses. This trend suggests a process of desorption, which is also observed in the LECA tests. As a remark conclusion, the

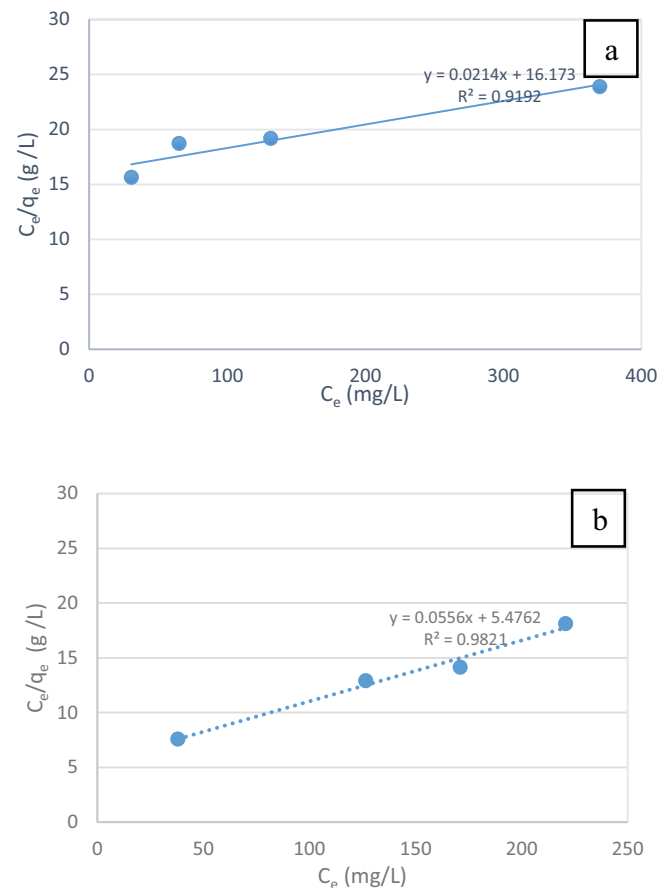


Fig. 8. Langmuir adsorption isotherm on experimental data, at  $T = 25^\circ\text{C}$ ,  $\text{pH} = 7$ ,  $V = 50$  mL,  $L = 10$  g/L, and different  $C_0$  for (a) LECA and (b) for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

Table 6  
Isotherm parameters for Langmuir and Freundlich models

	Model					
	Langmuir			Freundlich		
	$q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_F$ (mg/g)	$n$	$R^2$
LECA	31.84	0.0019	0.91	1.76	4.07	0.90
$\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$	4.31	0.01	0.98	1.38	1.87	0.97

results indicate that  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  demonstrates greater potential for nitrate removal than LECA. However, its production process is both costly and time-consuming.

### 3.4. Adsorption isotherm for LECA and $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$

To estimate the adsorption isotherms, several separate tests was performed for both LECA and  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  at pH  $\sim 7$  and 25°C. The data obtained at the equilibrium stage of the tests at the half an hour contact time, were applied to derive the Langmuir and Freundlich parameters. The linear plot of  $C_e/q_e$  vs.  $C_e$  shown in Fig. 8, indicate the applicability of Langmuir adsorption isotherm. Employing Eq. (5), values of  $q_m$  and  $K_L$  were calculated from the slope and the intercept of the line in Fig. 8a for LECA and 7b for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . The estimate of the model suggest the maximum uptake value  $q_m$  of 46.72 mg-nitrate/g of LECA and 17.98 mg-nitrate/g of  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . Energy of sorption value  $K_L$  of 0.0013 L/mg for LECA and 0.010 L/mg for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . The value of  $r$  was found to be 0.88 for LECA and 0.5 for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . Although, both materials showed favourable adsorption in early contact time, the parameters indicate a higher adsorption capacity for LECA in compare to  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ .

In the case of Freundlich adsorption isotherm model, the value of  $K_f$  is 1.76 mg/g for LECA and 1.38 mg/g for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  while  $n$  is 4.07 for LECA and 1.87 for  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ . The higher values of both parameters indicate higher adsorption capacity for LECA. Overall, the Langmuir isotherm showed a better agreement with the equilibrium data for both the LECA and the  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  adsorption. Table 6 summarizes the isotherm parameters for Langmuir and Freundlich models.

## 4. Conclusion

This study investigated the efficacy of LECA and its iron oxide-doped variant ( $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$ ) in treating nitrate contamination in water. The duration of contact emerged as the most critical factor influencing the removal process and efficiency. Interestingly, the removal rate declined as the contact time extended. Despite high adsorption levels at the initial stages of the contact period, a decrease was observed shortly due to the desorption phenomenon. The effect of adsorbent dosage on removal efficiency also exhibited a counter intuitive trend, with higher doses of adsorbents resulting in reduced nitrate removal. As for pH, neutral conditions slightly outperformed a pH of 4.5

in terms of adsorption. Although  $\alpha\text{-Fe}_2\text{O}_3\text{@LECA}$  demonstrated superior adsorption compared to LECA, desorption over time also diminished its potential. In conclusion, given the rapid desorption of nitrate ions, which is not desirable for practical use, further research on these adsorbents could shed light on their practical efficiencies in treating other unwanted substances.

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