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Nitrate adsorption by fired clay in fixed bed column

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Abstract

Excessive use of nitrogen fertilizers has increased nitrate concentrations in groundwater, which poses a health hazard from nitrate-contaminated drinking water and contributes to eutrophication. Nitrate removal from water systems has been carefully studied; However, new, low-cost solutions are urgently needed. Clay and terracotta minerals are commonly used in environmental applications due to their non-toxicity, global availability, low cost, and physical and chemical properties (ion-exchange capacity, high surface area, high adsorption, and catalytic properties). Although most are used to reduce cationic pollutants, depending on the method of modification or the materials with which they are mixed, they can be equally effective in removing anionic contamination. The goal of the study is to treat water containing excessive concentrations of nitrates to produce water of acceptable environmental specifications and to evaluate the performance of fired clay as a low-cost and environmentally friendly water treatment material.

Keywords: Adsorption;fire clay; nitrate; Bed depth column

الخلاصة: أدى الاستخدام المفرط للأسمدة النيتروجينية إلى زيادة تركيزات النترات في المياه الجوفية ، مما يشكل خطراً على الصحة من مياه الشرب الملوثة بالنترات ويساهم في التخثث. تمت دراسة إزالة النترات من أنظمة المياه بعناية ؛ ومع ذلك ، هناك حاجة ماسة إلى حلول جديدة منخفضة التكلفة. تُستخدم معادن الطين والتراكوتا بشكل شائع في التطبيقات البيئية نظرًا لعدم سميتها ، وتوافرها العالمي ، وانخفاض تكلفتها ، وخصائصها الفيزيائية والكيميائية (قدرة التبادل الأيوني ، ومساحة السطح العالية ، والامتصاص العالي والخصائص التحفيزية). على الرغم من استخدام معظمها لتقليل الملوثات الموجبة ، اعتمادًا على طريقة التعديل أو المواد التي يتم خلطها بها ، يمكن أن تكون فعالة بنفس القدر في إزالة التلوث الأنيوني الهدف من الدراسة هو معالجة المياه المحتوية على تركيزات زائدة من النترات لإنتاج مياه ذات مواصفات بيئية مقبولة ، وتقييم أداء الطين المحروق كمواد معالجة مياه منخفضة التكلفة وصديقة للبيئة.

1. INTRODUCTION

The most important resource for all living things is water since without it, life as we know it would not be possible [1, 2, and 3]. Organic and inorganic compound pollution of water is a major public concern [4, 5, and 6].

While nitrate is relatively harmless to adults due to its rapid excretion by the kidneys, quantities larger than 10mg can be lethal to newborns under the age of six months. This, when combined with hemoglobin in the blood, forms methemoglobin, resulting in "blue baby syndrome," a disease " [7].

Increased residential and industrial activity has resulted in the release of numerous contaminants into the aquatic environment in recent decades. It is critical to develop a reliable and ecologically acceptable solution to remove these contaminants from wastewater. Adsorption is a straightforward, cost-effective, and long-term solution among current technologies. Clay compounds have recently gained popularity as adsorbents due to their abundance, ease of manufacturing, and efficiency. This class of chemicals can remove 99 percent of dyes, metals, and hazardous negative ions from a variety of solutions quantitatively [8].

Several different methods have been used to reduce the concentration of NO_3 in water and the most common are electrolysis [9], reverse osmosis [10], adsorption [11], chemical denitrification using unevalent magnesium [12], and zero-valent iron [13], and electrochemical (EC) [14]. Because of the low waste output and low operational cost, adsorption is the simplest, most effective, and most efficient of these treatment processes. Various organic and inorganic contaminants can be removed from water using the adsorption technique [15].

A wide range of low-cost adsorbents have lately been proposed to maintain nitrate removal capacity. Natural phyllosilicates, also known as clay due to their particle size, have the potential to be inexpensive adsorbents because of their accessibility and accessibility and have outstanding physicochemical consistency, structural, and surface qualities [16]. Many low-cost adsorbents have been discovered to be effective at removing pollutants, including fired clay and natural soils. These materials are low-cost and readily available in huge quantities in the area. In terms of cost, availability, and adsorption properties, burned clay (FC) as an adsorbent outperforms many other commercially available adsorbents. It's also natural and non-toxic.

Column adsorption is the most common type of adsorption method. A column of absorbent particles was filled, and a liquid containing at least one adsorbent component flowed through the packed layer. Adsorption begins at the entrance to the column and continues until the exit [17]. The mass transfer zone (MTZ) is defined as the active surface of the bed where adsorption occurs. The liquid enters the column from below, and the contaminated adsorbent is rapidly absorbed when it comes into contact with the liquid (Fig. 1). As a result, the fluid that exits the column is free of contaminants. When concentrations in the effluent stream are continuously assessed, leakage of the absorbable elements is detected as the mass transfer zone approaches the exit of the bed, yielding the "breakthrough curve" [18].

Figure 1 Photograph of the continuous (fixed bed) experimental unit.

2. METHODOLOGY (FIXED BED SYSTEM)

The fixed bed is a cylindrical column filled with an appropriate packing substance for the treatment purpose, with liquid and solid phase concentrations changing with time and bed position. The pressure drop required for fluid to flow along the column at the desired flow rate is the most important topic. The liquid will flow and disperse evenly from the top to the bottom of the column, wetting the packing materials in the process.

The operation method of this system is simple, and it can achieve high removal efficiency. It can also easily scale up the system's design from laboratory to industrial applications. The process in the fixed bed column is active because the mass transfer is appropriate due to the driving force that is established in the column, resulting in improved removal efficiency and discharge quality [19].

Among the most crucial factors affecting the performance of fixed-bed dynamic systems is the discharge concentration history. The time at which the effluent concentration hits the threshold value is known as the breakthrough time (BTC) for these concentration-time curves, which are also known as BTCs. Proper adsorption system design must be based on correct breakthrough curve predictions for a set of conditions. Although the fixed-bed mode is quite useful, the analysis is often difficult. The adsorbent efficacy obtained from the concentration effluent breakthrough curve is commonly recognized as S-shaped [20].

Despite the fixed bed's ease of use, numerous flaws have been observed, particularly those relating to the allocated time for the mass transfer zone in the bed to advance. Because the advancement of the mass transfer zone (MTZ) brings time into the design equations, as shown in Figure 2, the accurate design of fixed beds is problematic. If the period is long, the bed will be vast, and the column will need to hold a considerable volume of expensive adsorbent as well as a large pressure drop. Adsorption is an exothermic reaction, hence raising the temperature of the adsorbent may cause desorption [21].

The breakthrough time is said to have occurred when the discharge concentration reaches 5% of the inlet flow value. The adsorbent bed was exhausted when the Ce/Co ratio reached 95% [23].

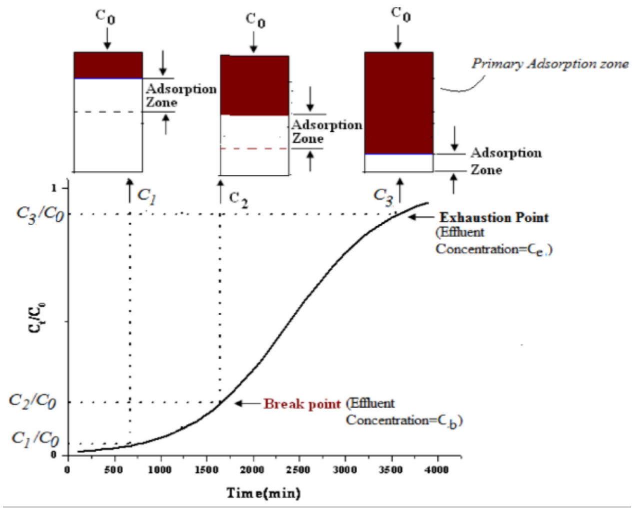

Figure 2 For a fixed bed, the development of the mass transfer zone (MTZ) and the breakthrough curve [22].

3. MATERIALS

3.1. Clay as Adsorbent

Clays are hydrous aluminosilicates that make up the colloid fraction (2 m) of soils, sediments, rocks, and water [24], and can be made up of a mix of fine-grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides [25].

Clays are significant in the environment because they operate as natural scavengers of contaminants, absorbing cations and anions by ion exchange, adsorption, or both. In an adsorption process, transferring a component from the gas or liquid to a solid phase is [26 and 27].

In general, The adsorption method has been selected because it method it is characterized by ease of operation and maintenance and achieves a high removal rate . A suitable sorbent material must be chosen to remove nitrates from the water, since the cost of the sorbent is the most important economic aspect of the adsorption process. Therefore, most researchers are working on developing a high-efficiency and cost-effective sorbent.Adsorption has been demonstrated to be the best water purification technique due to its many benefits. For many years, dangerous heavy metals have been successfully removed from aqueous solutions using clay and related minerals, which are plentiful and affordable. Different heavy metals can be removed from aqueous solutions using clay and related minerals, both in their natural and modified forms. Clay minerals can adsorb hazardous metals from water molecules because they have a lot of space between their layers. Most clays can inflate and widen the area between their layers to accommodate adsorbed water and ionic species [28].

To cut back on the use of pricey adsorbents, many clay adsorbents have been thoroughly investigated. The majority of the investigations reported maximum adsorption capabilities for specific pollutants using batch adsorption experiments, confirming their applicability and selectivity.

3.2. Potassium nitrate

Potassium nitrate is a crystalline solid that ranges in color from white to gray. soluble in water (the Physical properties of Potassium nitrate is shown in table below). It is non-combustible yet helps combustible materials burn faster. An explosion may occur if huge volumes of flammable material are engaged in a fire or if the combustible material is finely split. When exposed to heat or fire for an extended period, it may explode. In fires, toxic nitrogen oxides are created. It is used in solid propellants, explosives, and fertilizers [29].

Table 1 Physical properties of Potassium nitrate.

Formula	KNO_3
Molar Mass	101.1032 g/mol
IUPAC ID	Potassium Nitrate
Melting point	334 °C
Boiling point	400 °C
Density	2.11 g/cm³
Soluble In	Water, Ammonia, Glycerol
Appearance	White solid
Odor	Odorless
Density	2.109 g/cm3 (16 °C)
Melting Point	334 °C (633 °F; 607 K)

4. RESULTS AND DISCUSSIONS

4.1. Effect of Bed Depth

Different bed heights (10, 15 and 20 cm) packed with (0.5, 0.65, 1.27 kg) and particle size (0.6 mm) were employed to evaluate the influence of bed height on nitrate removal while other parameters were constant (i.e., beginning concentration = 10 mg/L, Q = 6 L/h, and pH = 6). Figures 3,4,5 and 6 show the nitrate adsorption curves on burnt clay particle material at various bottom depths a sample was taken every ten minutes for a period of 60 minutes. When the layer depth is lower, the percentage of nitrate removed rapidly reduces compared to when the layer depth is higher. The higher bed, on the other hand, requires more time to saturate due to the availability of a larger mass transfer surface for adsorption. There is also more space for clay particles in the higher layer's depth, which provides an additional number of binding sites for nitrate ions to be adsorbed. These findings are like those reached by [30, 31 and 32].

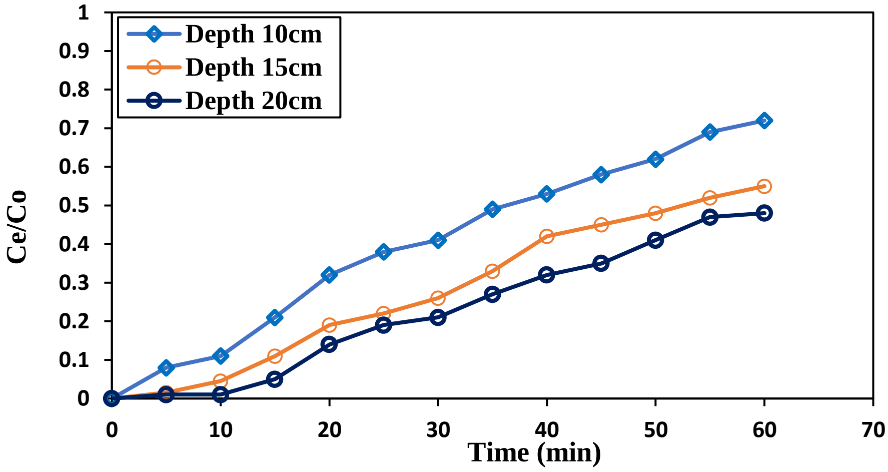

Figure 3 Fixed bed column absorption for nitrate ion adsorption on fired clay particles at various bottom depths at 30℃, (pH 6, Co = 10 mg/L, and Q = 6L/h).

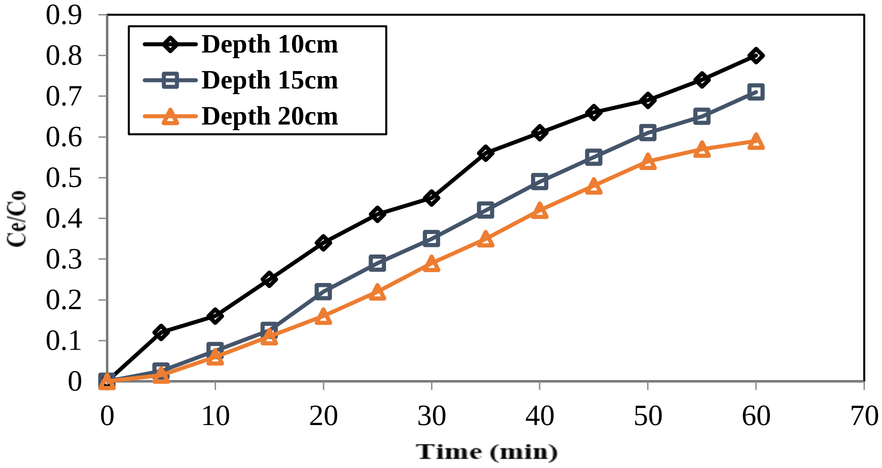

Figure 4 Fixed bed column absorption for nitrate ion adsorption on fired clay particles at various bottom depths at 30℃, (pH 6, Co = 10 mg/L, and Q =9L/h).

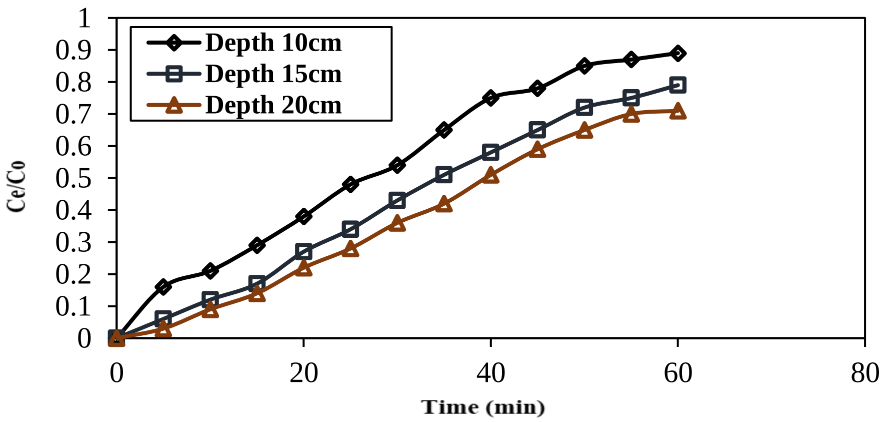

Figure 5 Fixed bed column absorption for nitrate ion adsorption on fired clay particles at various bottom depths at 30℃ (pH 6, Co = 10 mg/L, and Q = 12L/h).

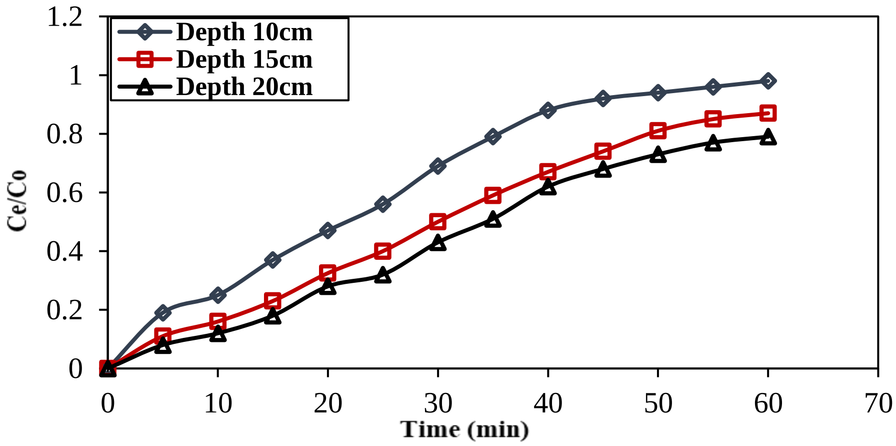

Figure 6 Fixed bed column absorption for nitrate ion adsorption on fired clay particles at various bottom depths at30℃ (pH 6, Co = 10 mg/L, and Q = 15L/h).

4.2. Effect of Flow rate

The influence of flow rate on adsorption performance was explored at flow rates of (6, 9, 12 and 15) L/h for initial nitrate concentration (10 mg/L), pH = 6 and bed depth (10, 15, and 20 cm), for treated water as shown in the figures 7,8 and 9 a sample was taken every ten minutes for a period of 60 minutes. It has been observed that the penetration time increases due to a rise in the contact hours between nitrate ions and the surface of the fired clay particles when the flow rate is sluggish. Furthermore, the higher the flow rate is, the lower adsorption is. Besides, the value of (C_e/C_o) was raised rapidly at higher flow rates since there is no enough time for nitrate ions to be adsorbed, which lowers the efficiency of adsorption. These results agree with those found by [33 and 34].

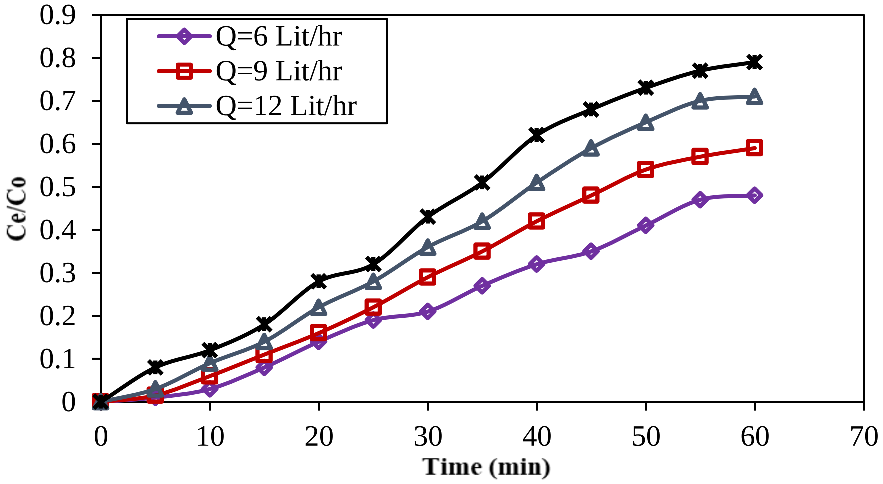

Figure 7 Fixed bed column breakthrough curves for nitrate ion adsorption onto fired clay particles at different flow rates (pH 6, Co=15 mg/L, and L=20 cm)

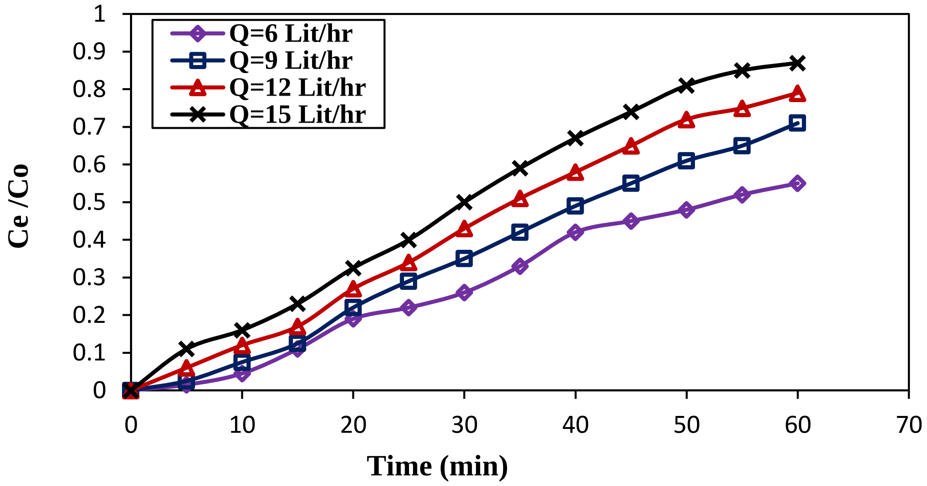

Figure 8 Fixed bed column breakthrough curves for nitrate ion adsorption onto fired clay particles at different flow rates (pH 6, Co=15 mg/L, and L=15 cm)

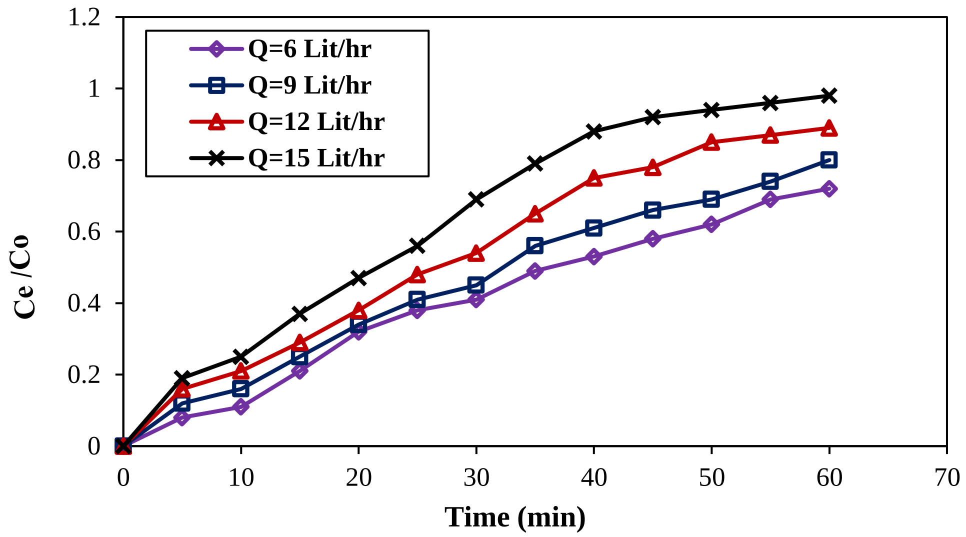

Figure 9 Fixed bed column breakthrough curves for nitrate ion adsorption onto fired clay particles at different flow rates at (pH 6, Co=15 mg/L, and L=20 cm)

4.3. Effect of Initial Concentration.

Using different concentrations (10, 20, 30 mg/L) with a flow rate (6 L/h) and a bottom height (10, 15, and 20 cm) as shown in Figures 10,11 and 12 which represent the nitrate absorption penetration curves when fired clay for different starting concentrations a sample was taken every ten minutes for a period of 60 minutes. It is observed that when the initial nitrate concentration increases, the adsorption capacity increases, and saturation is reached in a shorter time. The reason is that the adsorption binding sites are rapidly filled with increasing nitrate concentration. The results were similar to those obtained by [30].

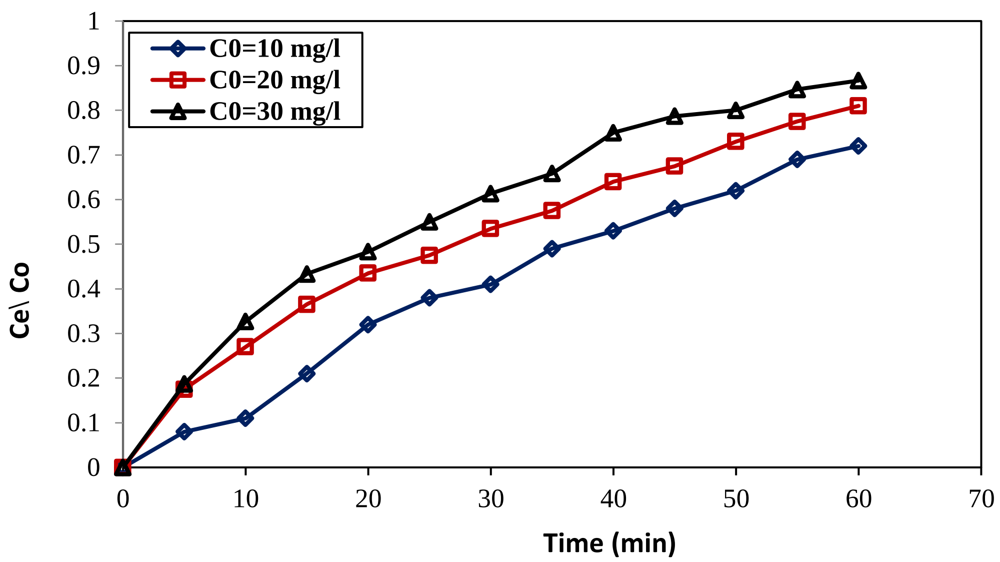

Figure 10 Breakthrough curves of the fixed bed column for nitrate ion adsorption onto fired clay particles at different initial concentrations (30℃, and pH = 6, Q= 6 mg/L, and L = 10 cm).

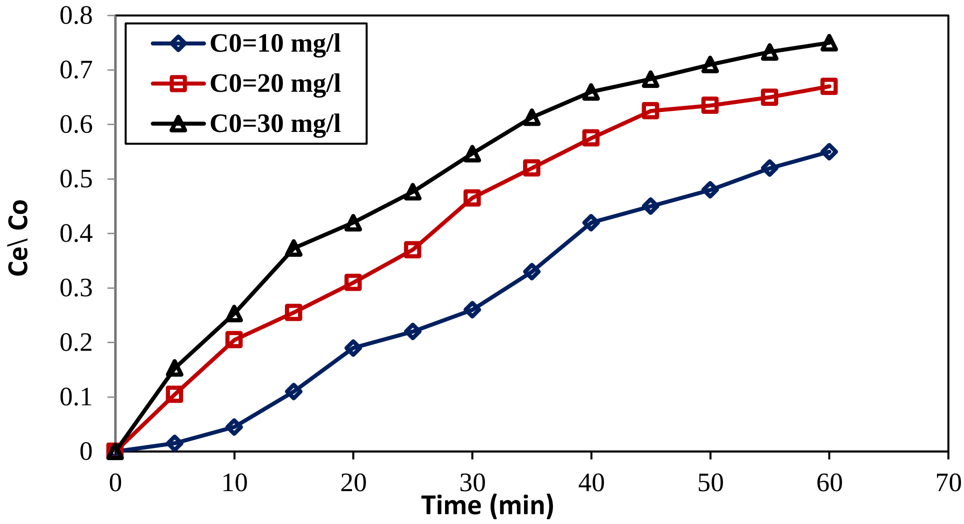

Figure 11 Breakthrough curves of the fixed bed column for nitrate ion adsorption onto fired clay particles at different initial concentrations (30℃, pH = 6, Q= 6 mg/L, and L = 15 cm).

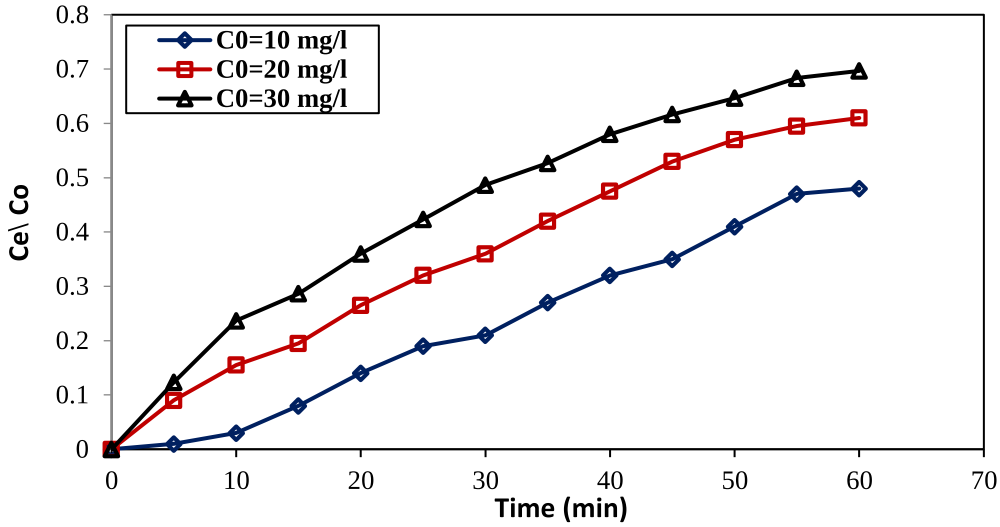

Figure 12 Breakthrough curves of the fixed bed column for nitrate ion adsorption onto fired clay particles at different initial concentrations (30℃, pH = 6, Q= 6 mg/L, and L = 20 cm).

5. CONCLUSION

Fire clay was used to remove nitrate from aqueous solutions by a continuous fixed bed column method on the performance of the adsorption column, and the effects of process variables including bed depth, flow rate, and initial nitrate concentration were examined. The study showed that when the bed depth increases from 10 cm to (15 and 20 cm), the percentage of adsorption increases by about 10% to provide a sufficient surface area for the adsorption process, but when the flow rate increases from 6 l\h to (9 ,12 and 15 l\h) , the removal efficiency decreases and the absorption decreases about 10% , because there is not enough time to absorb the nitrate ions. Also, when the nitrate concentration increases, the removal efficiency decreases because the adsorption binding sites fill up rapidly with increasing nitrate concentration, leading to saturation being reached in a shorter time. Finally, the study proved that the proud clay material is highly efficient in removing nitrates with a removal rate of more than 90% , and it is considered one of the low-cost materials .

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