ADSORPTION STUDY FOR THE REMOVAL OF NITRATE FROM WATER USING FIRED CLAY

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Abstract

This study focused on using adsorption process to eliminate nitrate ions from a synthetic water using fired clay (FC) materials as a low-cost adsorbent and to assess its performance and practicability as a complementary factor to eliminate nitrate ions in aqueous solution. The tests were implemented to explore the adsorption isotherm of nitrates at room temperature, the influence of many factors: the mass of adsorbent, contact time, agitation speed, pH, and primary adsorbate concentration has investigated. The findings demonstrated the nitrates reduction percentage was 93% for fired clay at best experimental conditions: pH=6, adsorbent dose 5 g, adsorbate concentration 10 mg/l, contact time 2.5 hours, and agitation speed 250 rpm. Langmuir and Frendlich isotherm models were applied to examine the experimental results. Results revealed that Langmuir adsorption isotherm was the preferred model for the nitrate adsorption onto fired clay material. This study obviously demonstrates the possibility of fired clay particles as low-cost adsorbent to remove nitrate from water.

Keywords: Adsorbent, Adsorption, Fired clay, Isotherms, Nitrate removal.

1. Introduction

Nitrate is polyatomic ion of nitrogen existing in water and soil. It is considerably soluble and results colourless, odourless, and tasteless water. It is extremely essential for plants and therefore nitrate is feasible in fertilizers useful to the plants. Nitrate is too water solute and surplus nitrate penetrates over soil system and enters groundwater table. Certain of the geological configuration as well consist nitrate ions, which raises groundwater nitrate in such places.

The nitrate ions in water change in divergent locations some areas greater than the drinking water standards. Most of the pollution in groundwater results from extreme usage of the manures and incorrect septic tanks. Some proportion also results from the plant metabolism activity of fixation. The supply can be indicated as below:

- Decomposing plant or animal matter.
- Agricultural manures and nutrition.
- Household sewage, septic tanks.
- Places of large intensity animal incarceration.
- Geologic materials including soluble nitrogen products.
- Normal cycle of nitrogen by plants.

Utilization of surplus nitrate polluted water does not direct to unexpected unfavourable results. Nitrate, when spent, acts with haemoglobin and decreases the oxygen in the body causes many diseases [1]. Nitrates in food and potable water are also involved in the production of carcinogenic nitrosamines [2]. Correlated to bio denitrification, adsorption is justified as one of the highest auspicious ways for nitrate removal outstanding due to simple process, easiness of design, and large performance [3]. Adsorption process confirmed by both the WHO and U.S. EPA as the greatest convenient techniques to remove NO_3 from liquiform methods [4]. There are several operations and methodologies utilized for nitrates removal; Adsorption and membrane processes are the majority noticeable ones [5], Moreover, chemical [6], and microbiological denitrification membrane bioreactors [7], and electrocoagulation [8]. Adsorption methods do not need highly advanced technologies, design features or processes to operate effectively. Adsorption technology has been used for the removal of organics [9], heavy metals [10], dyes [11] and several inorganic anions such as fluoride [12], and nitrate [13].

Adsorption is a process of adherence of ions or molecules from one stage into another. Traditional and non-traditional substances depended on a miscellany of several fundamentals are appropriated to NO_3 reduction from water. In the adsorption operation, absorbent cost is greatest essential economic element in the operation [14]. Recently, a huge number of cost-effective adsorbents have been stated to keep nitrates removal capacity. Natural phyllosilicates, normally recognized as clay because of their particles size, have the possible to act as alternative low-cost adsorbents because they are commonly available, accessible and a very good physicochemical constancy and structural and surface properties [15]. Fired clay and natural soils are amongst the enormous number of cost-effective adsorbents which have been recorded to possess pollutants removal capability. Those materials are cheap and are locally available in a huge amount.

The use of fired clay (FC) adsorbent has benefits over lots of other commercially available adsorbents in term of low-cost, a substantial availability,

excellent adsorption properties, non-toxic natural. The aim of this paper is to use fired clay as an absorbent to remove nitrates from drinking water. The current examinations are concentrated on the following issues:

- Adsorption behaviour of nitrate using local fired clay, including isotherms studies in batch tests.
- The effect of initial nitrate concentration, detention time, adsorbent dosages, and pH of solution on adsorption process.

2. Methodology

2.1. Adsorbate and adsorbent

In the present study nitrate was adopted as adsorbate. A stock solution of 1000 ppm nitrate was adjusted by melting potassium nitrate (KNO_3) in distilled water. Occupy unique physiochemical properties. In fact, clays are abounding, and they represent Nitrate stock solution of 1000 ppm was adjusted by melting 1.647 g of potassium nitrate in one litre of distilled water. A certain amount of the stock solution was mixed with distilled water to prepare the standard solution of each experiment to the required concentration. Fired clay (FC) were picked up from local marketplace and after that grinded down by hand into particles. The particles were filtered using the American sieve standards in the sanitary laboratory of Wasit University/College of Engineering. Then, particles were completely cleansed at various periods with purified water to extract contaminants and dehydrated by exhibition to the sun rays for 24 hours. Particle size choice was done and size with (1 mm) in diameter were chosen for nitrates reduction. The surface area of the fired clay (FC) is (2 m^2/mg).

2.2. Procedure of experiments

In the present study, adsorption experiments were performed by batch system into 250 ml flask on the magnetic agitator with 250 rpm. To control tests in separate environments, several factors as pH, detention period, adsorbent amount and primary dosage of nitrate were considered. The initial concentration of nitrates was 10 mg/l at contact time 2.5 hours. The total examinations were frequented triple times and average was dependent. At the end of each test, for both adsorbents, solution spread from Whitman 42 filter paper to isolate adsorbing particles from the solution, and then mass of NO_3 in the filtrate by 220 nm by spectrophotometer (Spectro Direct model Lovibond-Germany) read. The lab examines actions of several parameters with measured exchange parameter and other parameters kept constant. At the ending of each experimental, by deciding the optimum values, investigation the other influence of the other parameters will be followed.

2.3. Adsorption isotherm

The relation within the mass of adsorbed material (q) and the mass of the material in liquid stage (C) at temperatures (T) is adsorption isotherm. The greatest approved hypotheses to clarify the adsorption operation that had been articulated involve Langmuir equation and Freundlich equation.

To dictate the adsorption isotherms, Langmuir and Freundlich isotherm ideas linear configurations adopted to investigate NO_3 adsorption. Linear configuration of Langmuir model is defined utilizing the common Eq. (1): [15]

$$\frac{1}{q_e} = \frac{1}{C_e k_L q_{max}} + \frac{1}{q_{max}} \tag{1}$$

In Eq. (1), q_e is adsorbed NO_3 per unit mass of adsorbent as a function of (mg/g) and may be achieved from the common Eq. (2)

$$q_e = \frac{C_i - C_e}{m} \times V \tag{2}$$

where Ci is primary NO_3 mass in mg/l, m is adsorbent mass in grams and v is the volume of solution in litres. Ce is equilibrium mass of adsorbed material in liquid state after adsorption regarding mg/l, k_L and q_{max} are the Langmuir coefficients gained by plot $\frac{1}{q_e}$ versus $\frac{1}{C_e}$, this will be gained by plotting a linear line whose gradient is $\frac{1}{k_L q_{max}}$ and intercept is $\frac{1}{q_{max}}$

Linear form of Freundlich formula may be represent utilizing the Eq. (3) [16].

$$\log q_e = \log K_F + \frac{1}{n} \times C_e \tag{3}$$

In Eq. (3), q_e is quantity to absorb at the equanimity regarding mg/l, C_e is absorbed mass equanimity concentration with regard to mg/l and K_F and n are Freundlich coefficients gained by plotting $\log q_e$ versus $\log C_e$. Obtained by plot straight line with a gradient of and intercept of $\log K_F$ is found.

3. Results and Discussion

3.1. Point of zero charge, PZC

The specimens around (0.5 g) of fired clay were added to cone-shaped containers that include 60 ml purified water addition to 40 ml of (0.1 mol/l NaCl solution), after that staggered for 24 hours. Primary pH (2,3,4,5,6,7,8,9,10,11,12,13) were modified utilizing NaCl or HCl. After 24 hours, the terminal pH is calculated and the variation within the primary pH rates and the terminal pH rates were attained as illustrated in Fig. 1. The optimum pH is detected from the interruption point of zero with the graph that achieved by plotting (ΔpH against primary pH) [17]. From the Fig. 1, the pH$_{PZC}$ of pH for fired clay is 6.

3.2. Effect of pH

The adsorption technique was studied at pH ranged from 2 to 13, (the initial nitrates concentration was 10 mg/l, agitation speed 250 rpm, temperature 20ºC, and adsorbent dosage 5 g/100 ml). The results are illustrated in Fig. 2. The findings verified that the removal of nitrates increased when the pH of the suspension increased and achieved the greatest at pH 6, after that depressed with additional increasing in pH value. The adsorption of nitrate is likely preferred in low pH solutions since anion adsorption is joined with release of hydroxide OH⁻ ions.

The dependence of pH for nitrates sorption onto fired clay particles may be attributed to pH $_{PZC}$ as shown in Fig. 2. When pH of the suspension is lower than pH$_{PZC}$, the overall charge on adsorbent surface of fired clay particles is positive due to the adsorption of surplus hydrogen ion, which is preferred for nitrate adsorption owing to coulombic attraction. On the other hand, when pH of the solution is higher

than pH_{PZC}, then the overall surface charge is negative because of the desorption of H^+ and nitrate adsorption must engage with columbic repulsion.

For this reason, a reasonable removal of nitrates below pHPZC can be observed due to the existence of positively charged positions on the fired clay surface. At the low pH ranges, the quantity of nitrates adsorbed is decreased, this may be due to the existence of nitric acid HNO_3 which lowered the availability of free nitrate ions to be adsorbed as well as HNO_3 reduces the coulombic attraction between nitrate and the fired clay surface, HNO_3 is formed at a pH below 4. In the range of pH (8-13) as shown in Fig. 2, there is a decrease in the removal efficiency even though the surface is positively charged these behaviours can be attributed to the large competitiveness between nitrate ions and hydroxyl ions for fastened onto functioning sites. These results are consistent with many results achieved by several researchers for various type of adsorbents such as [1]. It is interesting to observe that the final pH (after adsorption) of the nitrates suspension with fired clay particles is near to 10.98 when the initial pH was (3 to 11), which indicates a presence of a large number of exchangeable OH-. This behaviour has been reported by [2].
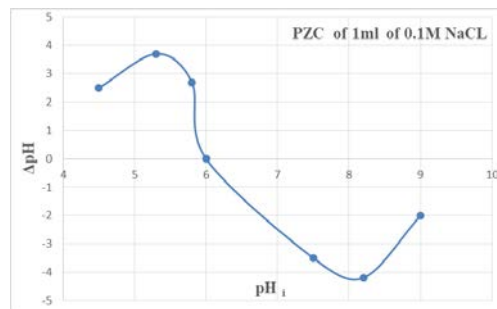

**Fig. 1. Point of zero charge of fired
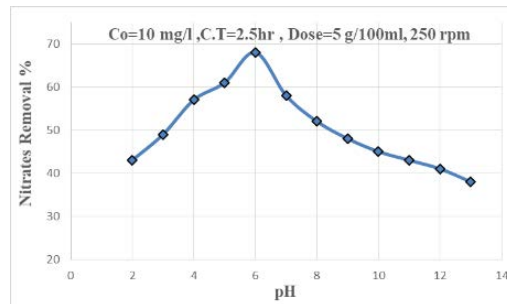clay articles by adding 1 ml of 1 M KCl.**

**Fig. 2 Nitrate ions adsorbed onto
fired clay particles at 20°C at different pH.**

3.3. Effect of agitation speed

Figure 3 shows the removal efficiency of nitrate ions adsorbed onto fired clay (FC) particles at different agitation speeds. It was demonstrated that the removal effectiveness of nitrate ions was increased when the agitation speed increased up to 250 rpm. This may be due to the certainty that when the speed becomes higher, the

thickness of layer will be decreased. It is clear from Fig. 3, there was reduction in the performance removal after 250 rpm which can be attributed to the adhesion of ratio from fired clay on the inner surface of volumetric flask at the mixing period, which decreases the adsorption of nitrate ions. So, 250 rpm will be fixed for all the next experiment because it was the optimum value that achieved optimum nitrate removal.

3.4. Effect of adsorbent dose

The impact of fired clay particles dosage on nitrates removal for an initiative nitrate's dosage of 10 mg/L, pH 6 and contact time of 10 hours has been studied as shown in Fig. 4. The performance of removal for nitrates ions increased from 22% at adsorbent dosage of 0.5 g/ 100 ml to 92% at adsorbent dosage of 5 g/100ml. and at the same time, it was notice that the adsorption capacity (*qe*) declined from 0.425 to 0.18 mg/g. The increase in nitrates adsorption with increase the amount of adsorbent mass can be attributed to large number of effective sites to adsorbed nitrates. It is clear that after a dosage of 5 g/100ml, the removal of nitrates decreases to of 91% because the large quantity of adsorbent filled most of the active site and led to decrease in net surface area of the adsorbent. Therefore, the amount of 5 g/100 ml of fired clay was appropriate to achieve the optimum performance of nitrate removal, and this amount will be fix for the next experiments.
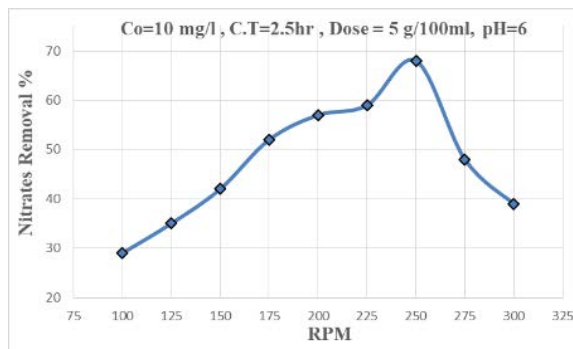

Fig. 3. Nitrate ions adsorbed onto fired clay particles at 20°C at different rpm.
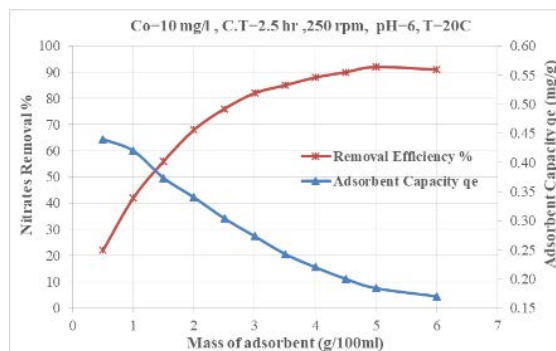

Fig. 4 Effect of fired clay particles dose on nitrates removal (pH 6, initial nitrates concentration= 10 mg/L. C.T=2.5 hrs, agitation speed).

3.5. Influence of contact time

The influence of collision period on nitrates reduction is illustrated in Fig. 5. The removal percentage of nitrates ions increases when the contact time increases. For the first half hour the performance of fired clay in nitrate removal was very fast and it was about 70% removal, and this behaviour may be due to large number of empty cavity sites on the surface of fired clay particles as well as the high initial concentration of nitrates at the initial condition. Then, this performance increased gradually from the 0.75 hour (73%) to reach maximum removal efficiency of 93% at contact time of 2.5 hours, resulting an effluent of nitrate concentration of 0.7 mg/l. For the last two hours of adsorption process the slope of performance removal was very low, indicating that the adsorption process was slow because as the time progresses the active sites on fired clay filled with the adsorbate.
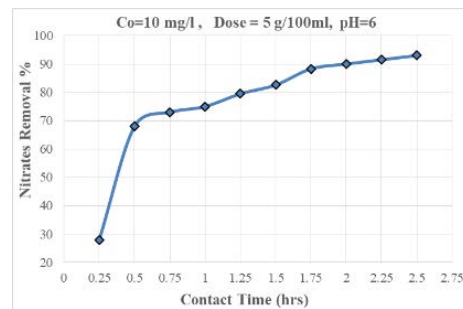

Fig. 5. Effect of contact time of fired clay on nitrates removal.

3.6. Constants of adsorption isotherm

Adsorption of nitrates ions onto fired clay particles in batch study has been achieved with initiative nitrates dosage of (10 mg/L) optimum operation conditions (pH=6, contact time 10 hours, adsorbent dosage 5 g/100ml and temperature of 20 °C), adsorption isotherm was achieved from drawing of adsorbent capacity (qe) versus equilibrium concentration of nitrates in the aqueous solution (Ce) as shown in Figs. 6, 7 and 8. Langmuir and Freundlich isotherm equations were examined to represent equanimity distributions of nitrates. The constants of the two models are presented in Table 1.
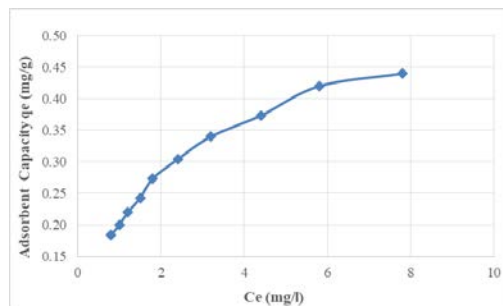

**Fig. 6. Adsorption isotherm of nitrates ions
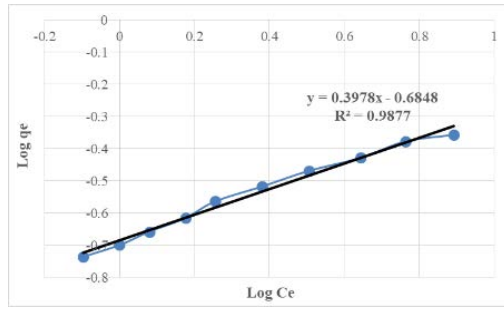onto fired clay particles at 20°C and pH=6.**
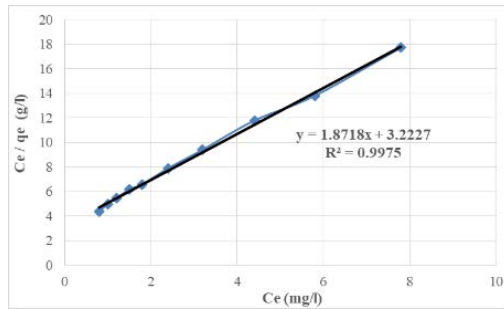
Fig.7. Freundlich isotherm.

Fig. 8. Langmuir isotherm.

Table 1. Langmuir and Freundlich isotherm constants.

Langmuir isotherm		Freundlich isotherm	
q_{max}	0.534	n	2.514
K_L	0.58	K_F	0.7
R^2	0.9975	R^2	0.9877

The equanimity information fitted well with fashion adsorption models. The better fit to the adsorption data for both models Langmuir and Freundlich model with the values of R equal to 0.9975 and 0.9877, respectively. It was observed that the value of adsorption intensity ($\frac{1}{n}$ =0.328) is less than unity, which implies that the nitrate adsorption process is favourable.

4. Conclusions

In this study, fired clay for the NO_3 reduction by adsorption investigated and the influences of pH, time of contact, mass of adsorbent, primary NO_3 concentration, and isotherms of adsorption in the NO_3 reduction operation studied. The findings demonstrated the possibility of using fired clay as an adsorbent to reduce NO_3 out of drinking water. When contact time increases the nitrate removal increases. And the most removal was done in the first 0.5 hour, then this performance increased gradually from the 0.75 hour (73%) to reach maximum removal efficiency of 93% at contact time of 2.5 hours. So that optimal contact time of 2.5 hours was concluded. Best pH for nitrate removal by fired clay was 6. As predicted, by increasing the mass of fired clay, the reduction of NO_3 increased. Adsorbent mass 5 g fired clay was approved as the optimum adsorbent mass. For fired clay

adsorbent by extending the primary NO_3 concentration, NO_3 reduction percentage increases and it may be realized that NO_3 reduction by fired clay is a physical phenomenon. Nitrate adsorption with $R^2 = 0.9977$ obeys the Freundlich isotherm demonstrating the adsorbed appropriate with Freundlich standard. NO_3 reduction by fired clay in ideal circumstances, 5 g adsorbent mass, collision period of 2.5 hours, pH=6.0 and primary concentration of 10 mg/l in 60 ml water and the NO_3 reduction percentage of 93% is done.

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