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Removal of Nitrate from Ground Water using Nigella Sativa

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Abstract: The goal of this study is to determine whether ground nigella sativa (GNS) can be used as a powerful adsorbent to remove nitrate from ground water. On nitrate adsorption, the effects of adsorbent dose of (GNS), pH, and contact time were examined. Ion chromatography was used to measure the concentration of nitrate ions in the ground water sample under various conditions both before and after equilibrium. The obtained results indicate that increasing the adsorbent dosage up to 0.5 g. and increasing the contact duration up to 150 minutes at pH 5. and 25°C will increase the removal percentage of nitrate. The adsorption characteristics of ground nigella sativa were assessed using the Langmuir and Freundich isotherms models. For the nitrate adsorption by Ground *Nigella Sativa*, it was discovered that Langmuir isotherms were more important than Freundlich isotherms.
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1. Introduction
1.1. Introduction and literature review

Nitrogen and oxygen combine to form the water-soluble ion known as nitrate salts. Nitrate can be found in the soil, water, plants, and air. Mainly from the breakdown of plant and animal wastes, which increases the amount of nitrate in our environment. Nitrate levels in the environment are also rising as a result of fertilizers [1-14]. One of the most prevalent contaminants in ground water is nitrate. When present in ground water at high concentrations, it has detrimental impacts on health. [2,3]. Agricultural activity, such as excessive application of inorganic nitrogenous fertilizers, runoff, and the discharge of sewage effluent and some industrial waste, causes nitrate to reach higher levels in both surface water and groundwater [4].

Due to its detrimental biological consequences, nitrate pollution of drinking water occurs in wells and groundwater. Due to these health dangers, high nitrate concentrations can reduce the blood's ability to carry oxygen throughout the body, which can result in a disease called methemoglobinemia, popularly known as "blue baby syndrome," which can be fatal. To lower nitrate concentrations to safe levels, effective treatment procedures need to be developed.[5,6,7]. A 50 mg/L NO_3^- nitrate limit standard for safe drinking water has been established by the WHO and the US Environmental Protection Agency (EPA) [8].

In dry and semi-arid areas, groundwater is the primary source of water supply [9]. About 0.61% of the fresh water supply in the world comes from groundwater [10]. There are two types of sources for contaminants in groundwater: point sources and non-point sources. It primarily comes from farmland that has been fertilized and pesticided [11]. The content of nitrates can be decreased using a variety of procedures, including ion exchange, reverse osmosis, electrodialysis, and adsorption methods [12].

The adsorption process is preferred over other treatment options due to its straightforward design, cost-effective operation, and success in removing nitrate when using a variety of adsorbent materials, including activated carbon made from olive stones, [13], chitosan, [14], red mud, [15], modified natural zeolite, [16], and cetylpyridinium bromide (CPB) modified zeolite. Mesoporous silica with ammonium functionalization [18, 19]. Recently, dangerous heavy metals as arsenate and arsenate were removed from waste water treatment using Nigella Sativa as a powerful adsorbent material [20]. Melon Peel is a new biosorbent created by Hikmatullah et al., with excellent biosorption efficiency and low cost of (Cu, Cd, and Pb) (II) from aqueous solution. [21].

Recently, Mohammed AL-Housni et al. removed nitrate from wastewater using an electrochemical approach [22]. To remove nitrate from drinking waters, Saeed Al-Marri et al. employed a new ultrasonic-electrocoagulation technique [23]. Table 1 [24] provides a thorough breakdown of Nigella Sativa's (NS) composition.

Table 1: The composition of Nigella Sativa:

Composition	**Moisture**	**Crude fat**	**Crude protein**	**Crude fiber**	**Ash**	**Total carbohydrate**
%	2.55	31.95	20.61	10.37	4.51	30.00

The goal of this study is to determine whether ground nigella sativa can be used as a reliable, inexpensive adsorbent for the removal of nitrate from ground water. With the help of ground nigella sativa, we also want to investigate the factors that influence the nitrate adsorption process.

2-Experimental.

2.1 Materials and Instrumentation

2.1.1 Preparation of Ground Nigella Sativa (GNS).

The Nigella Sativa was bought in Al- Madinah Al-Munawarah, Saudi Arabia (KSA), at a neighborhood market. It was ground into a homogeneous particle size in a grinder. After being thoroughly cleaned with distilled water to remove dirt, the ground Nigella Sativa was dried for two hours at 80°C to eliminate moisture. It was then kept in desiccators for a whole day.

2.1.2 Collection of the Groundwater sample.

An agricultural area in the Ali Wells neighborhood of Al- Madinah Al-Munawarah served as the source for the groundwater sample. As shown in Table 2, it was brought to the lab for physicochemical investigation.

2.1.3 Instrumentation:

Using an Ion Chromatography apparatus (Metrohm 881 compact IC pro-Anion MCS, Switzerland), characterized by a Conductivity Detector, the concentration of nitrate ions in the groundwater sample was evaluated both before and after equilibrium. cellular phase Sodium bicarbonate with carbonate of potash, flow rate: 0.800 ml/min. resin with anionic cation exchange. pH measurements are made with a pH meter (ADWA-AD8000). centrifuges (labofuges), employing a 10 minute cycle at 4,000 rpm. Dragon digital (hotplate), Shaking Water Bath (JSR, rpm-120, Temperature - 25Co), and Magnetic Stirrer.

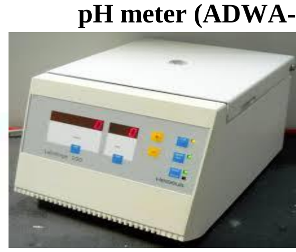
1.2.3.1 Ion Chromatography Instrument

For analyzing the chemistry of water, ion chromatography is utilized. Major cations including lithium, sodium, ammonium, potassium, calcium, and magnesium as well as major anions like fluoride, chloride, nitrate, nitrite, and sulfate may all be measured in the parts-per-billion (ppb) range using ion chromatographs. Ion chromatography can also be used to determine organic acid concentrations [25].

Ion Chromatography Instrument

pH meter (ADWA-AD8000)

Centrifuge



Shaking Water Bath

2.2. Procedures:

With various factors, experiments were run. First, we investigated the impact of ground nigella sativa dosage on nitrate adsorption. A glass sample tube was filled with various weights of ground nigella sativa (1g, 0.5g, 0.3g, 0.1g, and 0.05g), which were then mixed with a 10 ml sample of groundwater. Each glass test tube was shaken and maintained at 25°C (rpm-120) for 15 hours. Using a pH meter, solutions were adjusted for pH by stirring in 100 ml of ground water solution or sodium hydroxide or sulphuric acid solutions. To the best adsorbent dose (0.5 g), 10ml were added. 18 hours were spent shaking the mixes at 25 Co at (rpm-120).

Lastly, the influence of time on adsorption was investigated. At pH 5, the optimal adsorbent dose (0.5 g) was combined with groundwater sample (10 ml). At 25Co (rpm-120), the mixture was shaken. All of these variables go through a 10-minute centrifugation process before being diluted (50%), filtered, and added to an Ion Chromatography analysis.

The following equation [13] was used to determine the quantity of nitrate adsorption at equilibrium per unit mass of Ground Nigella Sativa (g), qe (mg/g):

$$qe = \frac{(Co - Ce)V}{W}$$

where *W* is the weight of the dry Ground Nigella Sativa utilized (g), Co is the initial concentration of Nitrate ions in the solution (mg/L), Ce is the equilibrium concentration of Nitrate ions in the solution (mg/L), and V is the volume of the solution (L). Additionally, as a result of this equation [13], the percentage of nitrate adsorption on ground nigella sativa changed as follows:$\% \, Removal = \frac{(Co-Ce)}{Co} x100$

3- Results and Discussion:

3.1 Ground Water Analysis:

Table 2 details the physiochemical properties of the ground water sample used in this study. According to the data, the water has a pH of 7.25 and a starting nitrate concentration of 65.3 ppm.

Table 2:- physiochemical investigation of Groundwater sample. At 25℃

physic-chemical parameters	Measurement
Initial nitrate concentration (ppm)	65.3
pH	7.25
TDS (ppm)	1200

3.2 Effect of Adsorbent Dosage:

The equilibrium nitrate ion concentration, Ce (mg/L), the quantity of nitrate adsorption per unit mass of (GNS), qe (mg/g), and the percentage of nitrate removed with various dosages of (GNS). (rpm,120) was estimated for 15h at 25°C and is displayed in Table 3. The dosage of Ground Nigella Sativa (GNS) and its impact on nitrate elimination are shown in Fig. 1. With increasing adsorbent dosage up to 0.5 g, it was shown that the elimination percentage increased to 96.214%. Because more adsorbent is used with a fixed initial nitrate concentration, there is a higher surface area and a greater number of accessible adsorption sites [22].

3.3 Effect of pH:

At the pH range of (2–9), the impact of pH value on the removal percentage of nitrate by (GNS) 0.5g was examined. According to Table 4 and Fig. 2, an acidic medium with a pH range of (4-6) results in a higher elimination percentage of nitrate. Increased protons in this acidic range, which result in positively charged sites on adsorbent surfaces, may be the cause of this behavior. However, it was noticed that as the pH rose to 9, the clearance % began to decline. This drop is brought on by the (GNS) surface being less active due to its positive charges, which reduces nitrate adsorption.

Table 3:- Effect of Ground Nigella Sativa (GNS) dosage on the equilibrium concentration of nitrate Ce, the amount of nitrate adsorption at equilibrium, qe and Removal% of Nitrate at 15h and 25℃ (rpm,120)

adsorbent weights of (GNS)	Ce (mg/L)	qe (mg/g)	% Removal
0.050 g	46.238	3.812	29.191
0.106 g	39.408	2.426	39.651
0.303 g	15.664	1.638	76.012
0.502 g	2.472	1.249	96.214
1.004 g	13.272	0.518	79.675

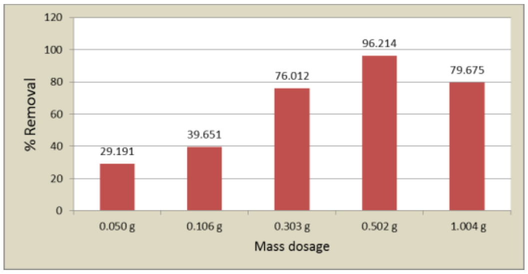


Fig 1- Effect of Ground Nigella Sativa (GNS) dosage on Removal% of Nitrate for 15h at 25℃ (rpm, 120), 0.01 L of ground water sample.

Table 4:-Effect of pH on the on the equilibrium concentration of nitrate Ce and Removal% of Nitrate by (GNS) 0.5g for 18h. at 25℃ (rpm,120).

pH	Ce (mg/L)	Removal%
2	7.016	89.256
4	0.310	99.526
5	0.268	99.589
6	0.318	99.512
7	2.311	96.461
9	12.864	80.300

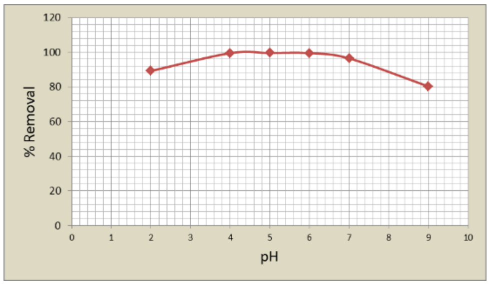


Fig 2. Effect of pH value on Removal% of Nitrate by (GNS) 0.5g for 18h at 25℃ (rpm, 120).

3.4 Effect of contact time:

Table 5 and Fig. 3 provide examples of the impact of contact time on the removal percentage of nitrate by (GNS) 0.5g. It was discovered that nitrate removal rises over time, reaching a constant amount at 150 minutes. Because there are more active adsorption sites available on the surface of (GNS), the rate of adsorption is increasing. The overlapping of active seats when the period exceeds 150 min may be the reason why the rate of adsorption reaches a constant state.

Table 5:- Effect of contact time on the equilibrium concentration of nitrate Ce and Removal % of Nitrate adsorption by (GNS) 0.5g and pH 5 at 25℃ (rpm,120).

Time (min)	Ce (mg/L)	Removal %
5	63.851	2.218
10	63.215	3.192
15	62.915	3.652
20	62.522	4.254
30	56.332	13.733
40	48.541	25.664
50	43.652	33.151
60	37.549	42.497
90	29.078	55.470
150	1.056	98.382
180	1.055	98.384

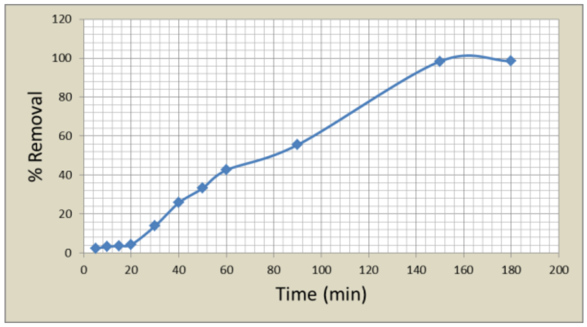


Fig 3: Effect of contact time on Removal % of Nitrate adsorption by (GNS) 0.5g pH 5 at 25℃ (rpm, 120).

3.5 Effect of Temperature

Table 6:- Effect of Temperature on the equilibrium concentration of nitrate Ce and Removal % of Nitrate adsorption by (GNS) 0.5g and pH 5-5.5 at 150 min (rpm,120).

Temperature ℃	Ce (mg/L)	% Removal
25	0.933	98.571
30	2.406	96.315
40	6.866	89.485
50	8.518	86.955

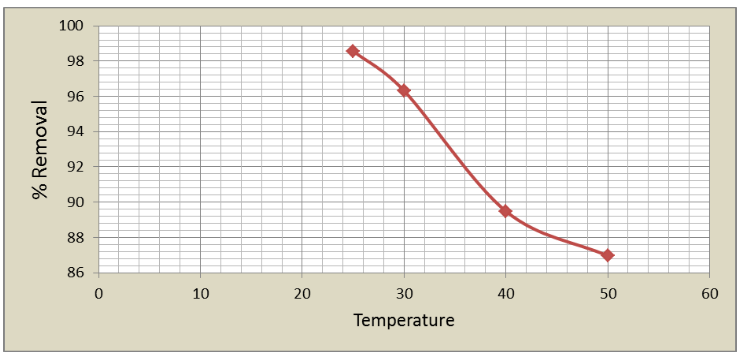


Fig 4: Effect of Temperature on Removal % of Nitrate adsorption by (GNS) 0.5g and pH 5-5.5 at 150 min (rpm,120).

3.6 Adsorption Isotherms:

In the current work, the adsorption characteristics of Ground Nigella Sativa were assessed using the Langmuir and Freundich isotherms models. This article aims to explain how the equilibrium concentration of nitrate in a water sample relates to the amount of nitrate that has been adsorbed.

3.6.1-Langmuir model:

According to the Langmuir isotherm, adsorption is homogenous and can only form monolayers when each molecule has fixed enthalpies and sorption activation energies. [26] provides the equation for the Langmuir isotherm in linear form.

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{1}{\text{Qo}}Ce$$

where Qo and b are Langmuir constants relating to adsorption capacity and rate of adsorption, respectively, and Ce is the equilibrium concentration of the nitrate (mg/L), qe is the quantity of nitrate per unit mass of Ground Nigella Sativa (mg/g), and so forth.

3.6.2-Freundlich model:

The equilibrium on a heterogeneous system is described by the Freundlich isotherm. Don't assume mono layer capacity from this point on [27]. Non-ideal and reversible adsorption is described by a recognized relationship that goes beyond the creation of monolayers. You can use this empirical model to create multilayer adsorption. The following Equation yields the Freundlich isotherm: [28].

$$\log qe = \log KF + \left(\frac{1}{n}\right) \log Ce$$

where Ce is the equilibrium concentration of the adsorbate (mg/L), qe is the amount of adsorbate per unit mass of adsorbent (mg/g), KF and n are Freundlich constants.

For different dosages of Ground Nigella Sativa, the characteristics of the Langmuir and Freundlich isotherms for nitrate adsorption are shown in Table 6. According to Figs. 5 and 6, the adsorption data was fitted to the Langmuir and Freundlich isotherms. The correlation coefficient, or R2, for Langmuir (0.9605) isotherms is found to be closer to 1 than for Freundlich (0.3152) isotherms. the adsorption method that fits Langmuir isotherms the best. In order for this study to follow Langmuir isotherms.

Table 7:-Langmuir and Freundlich isotherm models parameters of nitrate adsorption onto different Ground Nigella Sativa dosage. For 15h at 25℃(rpm,120)

adsorbent weights of (GNS)	Ce/qe	log qe	log Ce
0.050 g	12.129	0.581	1.664
0.106 g	16.239	0.385	1.595
0.303 g	9.561	0.214	1.194
0.502 g	1.977	0.096	0.393
1.004 g	25.616	-0.285	1.122

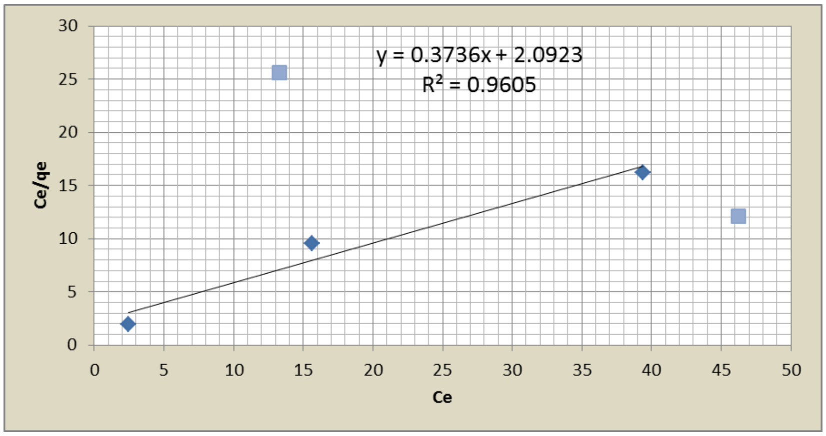


Fig 5 -Langmuir plot for nitrate adsorption onto different weights of Grinded different doses Nigella Sativa at(temperature: 25 ℃,(rpm-120) for 15h

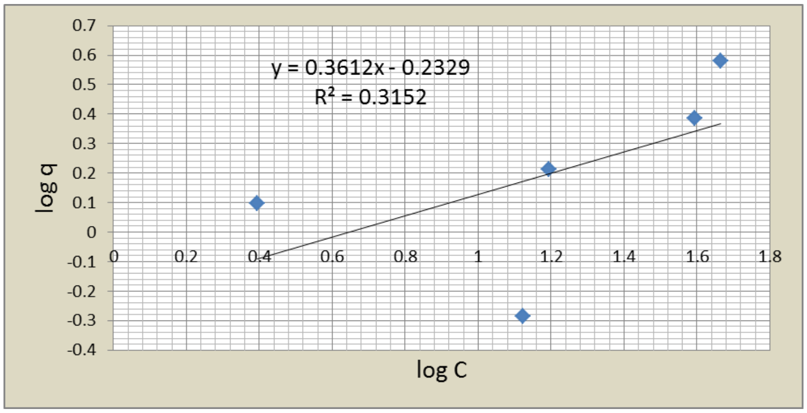


Fig 6-Freundlich plot for nitrate adsorption onto different weights of Ground Nigella Sativa at (temperature: 25℃, (rpm-120) for 15h.

4- Conclusion:

The findings of this study demonstrate the potential of ground nigella sativa (GNS) as a potent adsorbent for the removal of nitrate from ground water. The results showed that the greatest removal percentage of nitrate using (GNS) value was 99.589% under the following conditions: 0.5 g of adsorbent, 150 minutes of contact time, pH 5, and 25°C. It was discovered that the data fit Langmuir isotherms the best.

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