Olive Pomace as an Abundant, Low-cost Adsorbent for Nitrate Removal from Aqueous Solution

Abdounasser Omar1*, Maali Mahmoud Saed2, Maha Mohamed Abdalkarim2, Huwaydah Ahmed Iedeelah2, Wafa Beaj1
(1) Chemistry Department, Faculty of Science, Al-jabal Algharbi University, Gharyan, Libya.
(2) Undergraduate student, Chemistry Department, Faculty of Science, Al-jabal Algharbi University, Gharyan, Libya.
*Correspondence: abdounasseromar@yahoo.com

Abstract - Many methods have been applied in order to reduce nitrate concentration in aqueous solutions, among them is the adsorption onto the surface of agricultural wastes. In this study, batch experiments were carried out to investigate the adsorption of nitrate onto olive pomace (OP), a solid by-product of olive oil industry. To achieve this, six parameters were studied by varying only one parameter at a time. These parameters were the effect of: pH, contact time, temperature, adsorbent weight, agitation speed and nitrate concentration. The optimum pH was found to be 5, while the optimum time was 75 minutes. Nitrate removal percentage was found to increase with increasing adsorbent weight or temperature, with 92.5% of nitrate removed by using 2 g of OP and 48% of nitrate was removed at 60ºC. Generally, agitation speed increased the nitrate removal percentage, while high initial concentration of nitrate was found to decrease its removal percentage. These findings, combined with the low cost of OP and its abundance, suggest that OP is a potential adsorbent for nitrate removal provided that the optimum conditions are applied. Applying this method for nitrate removal will make drinking water safer to drink and wastewater safer to discharge.

Keywords: Nitrate removal, adsorption, olive pomace.

I. INTRODUCTION

Nearly 97% of earth's water is saline and 3% is fresh water [1]. Out of this 3%, about 70% of fresh water is frozen, 29% is present as soil moisture or as groundwater and less than 1% of the world's fresh water is in the lakes and rivers [2].

Because of its high water solubility, nitrate is one of the most common groundwater contaminant in the world, imposing a serious threat to drinking water supplies [3]. The accumulation of nitrate in the environment results mainly from: discharges of untreated municipal and industrial wastewater runoff septic tanks, processed food and meat products and decomposition of decaying organic matter buried into ground [4]. In addition, the heavy use of nitrogenous fertilizers is the main contributor to anthropogenic nitrogen in water [5]. Nitrates are soluble in water and do not bind to soil, so they migrate fast through soil, resulting into leaching of nitrates through soil into groundwater [6]. Although nitrate itself is relatively harmless, its conversion to nitrite or N-nitroso compounds in the body may produce toxic products [4] damaging the human body. For example, excess amounts of nitrate in drinking water may cause two adverse health effects: blue baby syndrome (methemoglobinaemia), especially in infants [7], and the potential formation of carcinogenic nitrosamines [8]. Formation of these compounds results from reduction of nitrates to nitrites, which then react in the stomach with amines to form a variety of N-nitroso compounds (NOC) [5]. The world health organization (WHO) has set a limit of 50 mg/L nitrate in drinking water, whereas the U.S. Environmental Protection (USEPA) has set a limit of 45 mg/L nitrate [9].
There are many traditional methods for nitrogen removal from drinking water, these include: physical processes (e.g. ammonia stripping) [3], biological processes (e.g. denitrification) [10] and chemical processes (e.g. breakpoint chlorination and selective ion exchange) [11]. The application of most of these methods on commercial scale is limited due to the high operational and maintenance costs. Comparatively, adsorption process seems to be a more attractive method for the removal of pollutants from aqueous solution due to its simple design and ease of operation [3]. Adsorption of nitrate from water could be the most promising technique in near future [2] for nitrate removal; that’s because of its simplicity, low cost and also the abundance of many materials that can be used as adsorbents.

Several agricultural products have been used as adsorbent, either directly or after being modified, for removal of chemical pollutants. Among these substances are: olive stones [12], banana peel [13], sugar cane bagasse [14], wheat straw [15], sunflower seed shells and rice husk [16], pine cone [17], almond shells [18], peach stones [19], miswak leaves [20], corn straw [21] and apricot stones [22].

In Mediterranean countries, the production of olives has been a major part of the agricultural products for many decades, with olive pomace (OP) as the main agricultural by-product of olive oil industry; for every 100 kg of olives, 35 kg of OP are produced. OP retains a small amount of olive oil and consists mainly of water, olive skin, olive flesh, fragments of pulp and pieces of kernels [23]. Chemically, OP consists of fiber (as cellulose), lignin and uronic acids along with oily wastes and polyphenolic compounds. It contains many polyvalent functional groups (e.g. hydroxylic groups) and anionic and cationic functional groups [24]. Like other agricultural wastes, OP has been used for removal of many chemicals including: heavy metals [25-27], phenols [28], textile dye [29].

As for nitrate, many studies have reported using agricultural products [30-33] for lowering its concentration in aqueous solutions. To the best of our knowledge, this is the first study to investigate the suitability of raw OP for nitrate removal from aqueous solutions. Compared to other adsorbents, OP has the advantages of being low cost, available in large quantities in Libya and that it contains many ionic groups which can interact with charged pollutants, thus enhancing the adsorption process. In addition to these advantages, OP contains many important polyphenolic compounds, which can be obtained by solvent extraction. These polyphenols have many applications related to health, including that they act as antioxidant, anti-inflammatory and antimicrobial [34]. This is also an economic benefit in addition of OP’s low cost.

The aim of these study was to lower nitrate concentrations in aqueous solutions by its adsorption onto OP surface. So, batch experiments were carried out to test a number of parameters known to affect the adsorption of nitrate by using OP as adsorbent, consequently the optimum conditions for these parameters were determined.

II. EXPERIMENTAL

All steps of adsorbent preparation, nitrate adsorption and analysis of remained nitrate were carried out at Gharyan’s Faculty of Science, Al-jabal Algharbi University, Gharyan, Libya. Solutions of nitrate, hydrochloric acid (HCl, 1M), sodium hydroxide (NaOH, 1M) and different concentrations of nitrate solution were prepared with double distilled water. Each adsorption experiment was repeated twice, at least, and the average of the adsorbed nitrate was calculated.
A. Chemicals
Toluene and ethanol used for extraction were of GPR grade. Sodium hydroxide and hydrochloric acid and sodium nitrate were of analytical grade. Reagents for nitrate analysis were purchased from Hach Company (Loveland, Colorado, USA).

B. Sampling and preparation of OP for the adsorption
A sample of 100 g of OP was collected into a clean plastic bag from an olive oil mill located in Gharyan, Libya, and then transferred to the lab where it was immersed into enough quantity of double distilled water for 15 minutes, followed by filtration. This was repeated for three times, and then the sample was dried at 100°C. Later, the dried OP sample was subjected to solvent extraction in soxhlet apparatus by using 2 mL of ethanol per 1 gram of OP for three hours. After the extraction was completed the OP was added to 180 mL of toluene in a conical flask and stirred for 10 minutes, filtered then dried, and finally washed with double distilled water and dried again.

C. Nitrate solutions
A stock solution of nitrate (1000 ppm) was prepared by dissolving 1.371 gram of sodium nitrate in sufficient water, transferred to a 1 litter volumetric flask and it was filled to the mark with double distilled water. This stock solution was used to prepare the other nitrate solutions for adsorption experiments.

D. Batch experiments
Batch experiments were carried out to investigate the effect of six parameters on nitrate adsorption onto OP, and this was performed by varying one parameter at a time. The investigated parameters included pH, contact time, temperature, adsorbent weight, nitrate concentration and agitation speed. Each set of experiments for each parameter were carried out simultaneously.

The effect of pH was studied firstly, then the other parameters. All adsorption experiments, except for the effect of the pH, were carried out in the same optimum pH, and for each experiment, HCl, and NaOH, solutions were used to adjust the pH of the solution.

All adsorption experiments were carried out in a 100 mL beaker sealed with a parafilm, and after the experiment was completed, the remained concentration of nitrate and the percentage of nitrate removal were determined.

- **The effect of pH**
The effect of pH on nitrate adsorption was investigated in the range 2–8. In a 100 mL beaker a 0.5 g of OP was weighed, and 25 mL of 100 ppm nitrate solution was added to the adsorbent. The pH of each solution was adjusted by 1M HCl or 1M NaOH then left at room temperature for 30 minutes. After 30 minutes the remaining nitrate concentration was determined.

- **The effect of contact time**
The effect of contact time was studied at room temperature for 30, 45, 75, 90, 105 and 120 minutes. The weight of OP in each experiment was 0.5 gram and the volume of the 100 ppm nitrate solution was 25 mL.

- **The effect of temperature**
The effect of temperature was studied at 20, 30, 40, 50 and 60º C. The weight of OP was 0.5 gram to which a 25 mL of 100 ppm nitrate solution was added. A water bath was used to control the temperature of the adsorption mixture till the contact time (30 minutes) was reached.

- The effect of adsorbent weight

To study the effect of adsorbent weight on the nitrate removal different weights of the adsorbent were used: 0.4, 0.8, 1.2, 1.6 and 2 gram. To each weight 25 mL of 100 ppm nitrate solution was added, and then the mixture was left for 30 minutes at room temperature.

- The effect of agitation speed

Three different agitation speeds were tried. Those were: 100, 200 and 300 rpm/min. Each adsorption mixture contained 0.5 gram of OP and 25 mL of 100 ppm nitrate solution. The contact time was 30 minutes for each experiment.

- The effect of nitrate concentration

Different nitrate solutions (100, 200, 300, 400 ppm) were used in order to investigate the effect of initial nitrate concentration. The volume of the nitrate solution, for each adsorption mixture, was 25 mL and the weight of OP was 0.5 gram. The contact time was 30 minutes for each adsorption experiment.

E. Real water sample

In order to test OP capacity for nitrate adsorption, nitrate concentration was determined in a real water sample collected from Gharyan’s public water supply, then aliquot of 25 mL of the sample was added to 0.5 g of OP in a 100 mL beaker. After pH adjustment to 5, the mixture was left for 30 minutes at room temperature and later analyzed for the remained nitrate.

F. Determination of adsorbed nitrate

After each adsorption experiment the remained nitrate concentration was measured with Hach colorimeter, model DR/900, according to the method described in the Hach Procedures Manual-Method (Method 8039) [35]. The method depends on the reduction of nitrate with cadmium metal to nitrite. In its turn, the nitrite ion reacts with 4-aminobenzenesulfonic acid (sulfanilic acid) to form an intermediate diazonium salt, which couples with 2,5-Dihydroxybenzoic acid (gentisic acid) to form an amber colored solution with an intensity related to the nitrate solution. The percentage of nitrate removal was calculated as follows: 100 (Ci-Cad)/Ci, where Ci represents the initial nitrate concentration and Cad represents the remained nitrate concentration after each adsorption experiment.

III. RESULTS & DISCUSSION

- Effect of pH

Because pH affects the surface charge of the adsorbent, the degree of ionization and the species of the adsorbate [36], so it was investigated before the other parameters. As shown in Fig. 1 the highest removal percentage of nitrate (45.6%) was at pH=5 while the lowest one (20.9%) was at pH=8. The decrease of removal percentage at the basic medium could be attributed to the competition between the nitrate and hydroxyl ion at the active sites of the adsorbent. These findings suggest that nitrate removal with OP favors weak acidic solutions. Results of other studies [3, 37], in which other adsorbents were used, have shown that the optimum pH for adsorption was 5.
Effect of contact time

From Fig. 2 it is obvious that the highest removal percentage of nitrate was 50.9 % and it was observed at 75 minutes.

The same figure shows that increasing the contact time from 30 to 75 minutes increased the removal percentage; however, after 75 minutes there was only a small change in the efficiency of nitrate removal. This can be attributed to the decrease of the active sites of the adsorbent which were available for adsorption. At the beginning there were many vacant active sites available for adsorption, but their number decreased after the equilibrium time was reached, because most of these sites became saturated with nitrate ions [38].

Effect of temperature

Fig. 3 shows that the lowest removal percentage was at 20ºC, while the highest one was at 60ºC. Raising the temperature three times from 20-60ºC nearly doubled the removal percentage, suggesting that the adsorption process is endothermic. And from the same figure, it is clear that removal percentage linearly increased with increasing of temperature.
It was found that increasing the adsorbent weight has the most appreciable effect on the adsorption process. Fig. 4 shows that increasing the adsorbent weight increased the nitrate removal percentage, and the maximum one was 92.5% when 2 gram of OP was used as an adsorbent dosage.

From the same figure it is clear that the removal percentage has increased nearly four times when 2 gram of the adsorbent was used instead of 0.4 gram. The reason for this is attributed to that increasing the adsorbent weight increases the number of the active sites available for adsorption, and also increases the surface area, and consequently increases the removal percentage. Similar explanation has been proposed in a study [39] about the removal of methylene blue by using activated carbon.

**Effect of agitation speed**

Fig. 5 shows that that highest removal percentage was 68% when the agitation speed was 100 rpm, which was the minimum agitation speed, while the lowest removal percentage was 28% and this was observed when the adsorption process was carried out without agitation.
Generally, the results reflect that stirring the adsorption mixture improved the adsorption of nitrate by OP. However, applying agitation speed of 200 and 300 rpm caused the removal percentage to decrease compared to a 100 rpm. Increasing the removal percentage with agitation resulted from the increase of the mobility of nitrate ions, and so they can reach the active sites in less time with enough numbers to adsorb. On the other hand, the decline of nitrate removal percentage when more speed of agitation was applied could be resulted from desorption of nitrate ions, or from getting more mobility for nitrate ions than the optimum one, resulting in lowering their ability to orientate into the proper position for adsorption to occur.

• **Effect of nitrate concentration**

Generally, using high initial concentration of nitrate was found to decrease its removal percentage Fig. 6 shows that nitrate removal percentage slightly increased with increasing the nitrate concentration from 100 to 200 ppm. The explanation for this is that there were enough vacant active sites on the adsorbent surface when the nitrate concentration increased to 200 ppm, and so more of nitrate ions adsorbed. Yet, increasing the nitrate concentration higher than 200 ppm resulted in lowering the removal percentage, which can be explained as follows: with increasing the initial nitrate concentration the number of nitrate ions in the solution increases, but the amount of adsorbent remained unchanged [40], so the excess of nitrate ions would not find enough active sites, and as a result of this, the removal percentage was lowered. In addition to this, increasing the nitrate concentration led to more competition between nitrate ions on limited active sites of the adsorbent causing the nitrate removal percentage to decrease.
Real water sample

For the real water sample the removal percentage was 31% which was close to the removal percentage (34%) for an artificial one with the same conditions. This could be considered a good percentage, particularly when taking into account that other negative ions exist in the real sample, and these ions compete with nitrate ions on the same active sites. In addition to that, except for pH, other conditions (like adsorbent weight and contact time) were not optimized.

IV. CONCLUSION

Controlling the parameters that affect nitrate adsorption onto OP enhances nitrate removal from aqueous solutions. And, by taking into account the obtained results of this study and the low cost of OP, as well as its availability, OP could be considered a good adsorbent for nitrate removal from aqueous solution provided that the optimum condition are applied. The application of this method for nitrate removal will make drinking water safer to drink and wastewater safer to discharge. Other studies could be conducted by treating OP with many chemicals (like sodium hydroxide, phosphoric acid, hydrogen peroxide, and potassium dichromate) in order to modify the functional groups found on OP surface. This may improve OP capacity for nitrate removal from aqueous solutions.

LIMITATION OF THE STUDY

This study was carried out by using the OP for adsorption without grinding and sieving which may have decreased the surface area, and so lowered the percentage of nitrate removal.

REFERENCES


