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Removal of nitrate from JUST wastewater effluent: a case study

S. Al-Asheh*, A. Al-Zoubi, H. Malas

Department of Chemical Engineering, Jordan University of Science and Technology, PO Box 3030, Irbid 22110, Jordan
Fax: +962 2 7209048; email: alasheh@just.edu.jo

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ABSTRACT

Eutrophication phenomena occurred at JUST constructed pond. The main reason of this eutrophication process is the wastewater effluent of the campus wastewater treatment plant. This is due high nitrate content of the water effluent. The objective of this project is to decrease the concentration of nitrate in the wastewater effluent of the campus wastewater treatment plant in an attempt to prevent the eutrophication process at the artificial pond. This is accomplished by use of adsorption process with newly developed adsorbents. Basically, two adsorbents were considered in this project, namely fly ash and banana peel. The effects of factors such as particle size, temperature and pH on adsorption process were investigated. From kinetic studies, equilibrium time was as short as 10 min. It was observed that pH plays an important role in the nitrate adsorption process. It was also observed that fly ash is more effective than banana peel in bench scale to remove nitrate. Adsorption isotherms for fly ash and banana peel were fitted to both Freundlich and Langmuir models. Fly ash and banana peel have potential of being used as sorbents for removal of nitrate from wastewater effluent of JUST wastewater treatment plant.

Keywords: Nitrate; Algae; Adsorption; Fly ash; Banana peel; Isotherms

1. Introduction

Water pollution is any chemical, physical, or biological change in the quality of water that has a harmful effect on any living organism that drinks or uses or lives in it. When humans drink polluted water it often has serious effects on their health. Water pollution can also make water unsuited for the desired use. One class of water pollutants is nutrients They are water-soluble nitrates and phosphates that cause excessive growth of algae and other water plants. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

Nitrogen and phosphorus are essential for healthy plant and animal populations, however, elevated concentrations of these nutrients can affect water quality, cause excessive growth of algae and other water plants. The process by which a body of water acquires a high concentration of nutrients, particularly phosphates and nitrates, is called *eutrophication*, where such nutrients typically promote excessive growth of algae. As the algae die and decompose, high levels of organic matter and the decomposing organisms deplete the water of available oxygen, causing the death of other organisms, such as fish. Eutrophication is a natural, slow-aging process for a water body, but human activity greatly speeds up the process [1].

*Corresponding author.

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Human activities almost always result in the creation of wastes, and many of these waste products often contain nitrates and phosphates. Nitrates are compounds of nitrogen, and most are produced by bacteria. Both nitrates and phosphates are absorbed by plants and are needed for growth. However, the human use of detergents and chemical fertilizers has greatly increased the amount of nitrates and phosphates that are washed into our lakes and ponds. When this occurs in a sufficient quantity, they act like fertilizer for plants and algae and speed up their rate of growth.

Eutriophication occurred at JUST constructed pond. Since it is affected by humans made effluents. An algal bloom is expected to happen resulting from excessive load of nutrient, calm conditions and less water inflow. The main sources of pond's water are both Wadi Hassan wastewater treatment plant (WWTP) and JUST wastewater treatment in addition to the rainfall water, which is confined to short period in winter and spring. JUST WWTP receives wastewater from different activities in the campus. It is expected that the increase of ammonium would increase nitrate content of water effluent.

Previous investigation showed that the main source for nitrate augmentation at the pond is the effluent of JUST WWTP [2]. Another previous investigation for determination of the source of nitrate content also showed that the two locations at JUST campus containing the highest ammonium concentration were the engineering and medical buildings [1]. It has also been shown that the ratio between nitrogen and phosphorous was high enough for eutriophication to occur, which means that the nitrate content in the effluent of JUST WWTP is the reason for eutriophication in the pond and thus an increase in the algal growth [1]. Therefore, if it is possible to decrease the nitrate concentration in the effluent of the bond, the eutriophication process can be suppressed in the pond. It is the objective of this project to find suitable method for reduction of nitrate content in the effluent of JUST WWTP, which represents the influent to the pond.

Many methods, either biological or physiochemical, are available for the removal of nitrate from wastewater. These include, nitrate degradation processes via biological processes (denitrification, nitrification), chemical processes (breakpoint chlorination, selective ion exchange), physical operation (ammonia stripping, electrodialysis, filtration, reverse osmosis) [3], catalytic nitrate reduction, and separation processes via distillation. Other operations or processes are conventional treatment (primary, secondary), biological processes (bacterial assimilation, harvesting of algae, oxidation ponds).

Adsorption is considered as one of the methods for removal of nitrate from wastewater; it becomes one of the most economic and effective methods. Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. Tremendous numbers of materials are available in literature for adsorption of nitrate from wastewater. Some of these materials include sepiolite, activated carbon, slag [3], coconut coir pith [4], and sugar beet [5].

The main objectives of this project are:

(1) To decrease the nitrate content in the effluent of JUST WWTP using adsorption process.
(2) To find new cheap adsorbent for nitrate, such as fly ash, strew and banana peel and compare the performance of these materials with activated carbon.
(3) Use the best adsorbent to study the effluent of such operating parameters as pH, temperature and dose concentration on the removal of nitrate from JUST WWTP effluent.
(4) To study the removal process using packed bed adsorption system as an attempt to implement such technique to the existing WWTP at the campus.

2. Materials and methods

2.1. Materials

Wastewater effluent from the campus wastewater treatment plant is the material under investigation. This plant receives wastewater from different activities in the campus. It is expected that the increase in ammonium would increase nitrate content of the water effluent. After measuring the concentration of nitrate for the different influents to the JUST artificial pond, it was found that the effluent from the wastewater treatment is the main source for nitrate augmentation in pond [2].

Fly ash is the solid material which is carried away from the power plant boiler in the flue gas during coal combustion. The properties of fly ash may vary considerably according to several factors such as the geographical origin of the source coal, conditions during combustion, and sampling position within the power plant. Fly ash particles are generally spherical in shape and range in size from 0.5 to 100 μm, but most fly ash particles are in the silt-sized range of 2–50 μm. They consist mostly of silicon dioxide (SiO_2), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed, and hazardous; aluminum oxide (Al_2O_3)

and iron oxide (Fe_2O_3) (Wikipedia, internet). Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides. The major elemental constituents of fly ash are Si, Al, Fe, Ca, C, Mg, K, Na, S, Ti, P, and Mn. Nearly all naturally occurring elements can be found in fly ash in trace quantities. Certain trace elements, including As, Mo, Se, Cd, and Zn, are primarily associated with particle surfaces. The fly ash that was used in the experiments has been collected as a residue of a household fireplace that maybe different in its properties and components than other types of fly ash [6].

2.2. Banana peels

Banana peels were collected from households. The peels were separated from the fruit gently, washed thoroughly, dried in sunlight, and then dried further in an oven at 90°C. Dried peels were minced into powder to be used further for the adsorption tests.

Banana peel constituted carbohydrates, proteins, lipids, and fibers. The work Castro et al. [7] provided the FTIR for banana peel. The FTIR obtained by those authors showed absorption bands of carboxylic and amine groups at 1,730 and 889 cm^{-1}, respectively.

2.3. Adsorption test

The batch adsorption tests have been conducted at different temperatures, namely 25, 35 and 45°C. In this case, water bath shaker was used and each time it was adjusted at specified temperature. Wastewater solution was prepared and initial concentration of nitrate was measure before use in the test. Then, certain amount of adsorbent was placed into flasks containing 100 ml of this solution in order to give a concentration of adsorbent in the final suspension in the range 5 to 25 mg/ml. The pH of the suspensions was adjusted in the range of 3–8 using either 0.1 M acetic acid or NaOH. The systems were maintained in a thermostatic liquid shaker at the desired temperature. At specified periods of time, samples were removed from the shaker for further analysis in order to investigate the kinetics of the process; otherwise they will stay until equilibrium. The samples were filtered and the nitrate concentration in the filtrate was measured using VS-spectrometer (GMBH, DR-5000, Germany). After that, the amount of nitrate adsorbed, or uptake, was calculated using the balance equation:

$$q = \frac{V(C_0 - C)}{m} \tag{2.1}$$

where C_0 is the initial concentration of nitrate in the solution (mg/l), C is nitrate concentration (mg/l) after adsorption, m is the amount of adsorbent (mg) been added, V is the volume of solution used (l), and q is the uptake (mg nitrate/mg adsorbent). To study the effect of different operating parameters on this process, in each experiment one parameter was varied while all other parameters were kept constant.

Nitrates were measured using Hach Lange VS-spectrometer (GMBH, DR-5000, Germany) with corresponding nitrate kit.

2.4. Effect of sorbent concentration

Different amounts of either adsorbent (fly ash, or banana peel), in the range 0.05–0.7 mg, were added to flasks containing 100 ml of JUST water treatment effluent of known initial concentration of nitrate. The mixture was agitated in a shaker for 10 min. Sorbent from the samples was separated by vacuum filtration through a 0.45 μm cellulose filter paper, and the filtrate was analyzed for nitrate using spectrophotometer (DR-5000). When samples of nitrate solution without sorbent, which served as blanks, were filtered, the concentrations of the nitrate were the same before and after filtration.

2.5. Effect of temperature

Effect of temperature was studied for both fly ash and banana peels to know how adsorption process will be affected. In this case 0.5 g of fly ash was added to 100 ml of waste water, the temperature of shaker was adjusted to either 25 or 35 or 45 °C. The mixture was agitated in shaker the sample was taken after 10 min (after equilibrium was attained), the sample was then filtered and the nitrate concentration was measured by DR-500 device.

2.6. Effect of initial pH

Waste water at different pHs were prepared, and adjusted using either the pH of these solutions was adjusted using acetic acid or NaOH (0.1 M). It was prepared seven samples of different pH values (3, 4, 5, 6, 7, 8, and 9).were prepared. Each sample contains of 100 ml and then 0.5 g of fly ash was added to each sample. The mixtures were agitated in the shaker and then samples were taken after equilibrium. The samples were filtered and concentration of nitrate was measured by DR-500 device.

2.7. Continuous adsorption process

Continuous adsorption process was carried out in a column packed with fly ash or banana peel as sorbent material. A 25 cm glass column was designed with two ends of the column fitted with cellulose filter paper, O-ring, and plug stoppers. The column was packed with 50 g (unless otherwise stated) of adsorbent. Treated water from JUST WWTP of a given concentration of nitrate was pumped upward through the column at a set flow rate. Samples were collected, continuously from the top of the column. This process was carried out until the column become saturated with nitrate under consideration (i.e. when the effluent and the influent concentrations are equal).

3. Results and discussion

3.1. Removal of nitrate by different adsorbents

Three types of adsorbents, namely barely straw, banana peel and fly ash were tested and compared with powder activated carbon. The concentration of nitrate of waste water was 13.8 ppm, and sorbent concentration of 5 mg/ml was used. The results are presented in Table 1. It is noted, in general, that this adsorption process is time dependent; the longer the contact time the more is the uptake. It is also seen that highest removal is achieved when using fly ash or banana peel and the least is when using activated carbon. Thus, banana peel and fly ash will be considered for further investigation to test their capabilities in removing nitrate from JUST wastewater effluent.

Table 1
Residual concentration and nitrate uptake for JUST wastewater effluent using different adsorbents

Adsorbent	Time (h)	Nitrate concentration (mg/L)	Nitrate uptake (mg/g)
Fly ash	19	1.9	2.38
	21	0.7	2.62
	24	0.0	2.76
Activated carbon (powder)	24	10.1	0.74
Straw	18	7.0	1.36
	20	4.3	1.9
	24	2.2	2.32
Banana peels	18	0.6	2.64
	20	0.0	2.76
	24	0.0	2.76

4. Sorption isotherms

The equilibrium isotherms are one of the most important data for adsorption considered in this work process and give the capacity of a sorbent for a sorbate. Isotherms can be obtained by examining batch reactions at fixed temperatures. Several isotherm equations are available and two important isotherms are selected in this study, which are the Langmuir and Freundlich isotherms. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L}\left(\frac{1}{C_e}\right) \quad (4.1)$$

where q_e is the equilibrium nitrate concentration on the adsorbent (mg/g), C_e the equilibrium nitrate concentration in the solution (ppm), and K_L is the Langmuir adsorption constant (L/mg) which is related to the free energy of adsorption. The K_L and q_{max} values can be obtained from the slope and the intercept, respectively, of the linear plot of $1/C_e$ vs. $1/q_e$.

The Freundlich isotherm is an empirical equation employed to describe heterogenic systems. A linear form of the Freundlich equation is:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \quad (4.2)$$

where K_F $\left(\left[\frac{mg^{(1-\frac{1}{n})}l^{\frac{1}{n}}}{g}\right]\right)$ and $1/n$ are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, or degree of sorption intensity, respectively. The $1/n$ and K_F constants can be obtained from the slope and the intercept, respectively, of the linear plot of $\ln C_e$ vs. $\ln q_e$.

Equilibrium data for nitrate were collected using fly ash and banana peel and using JUST Waste Water effluent with different concentrations. The collected data were represented by both types of models. The Langmuir and Freundlich plots are shown in Figs. 1 and 2, respectively, for the case of banana peel adsorption, while the parameters for both models are displayed in Table 2.

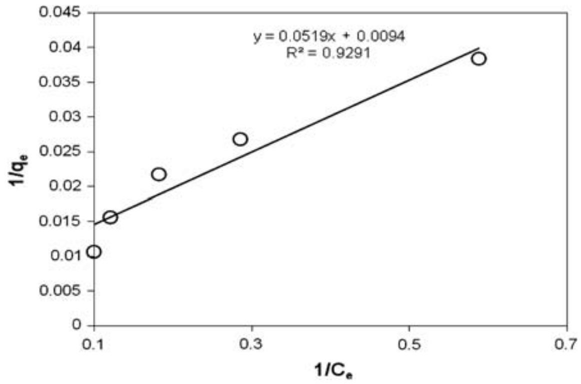

Fig. 1. Langmuir isotherms for the sorption of nitrate onto banana peels. Initial concentration of nitrate: 14.7 ppm; initial pH: 7.34; temperature: 25˚C.

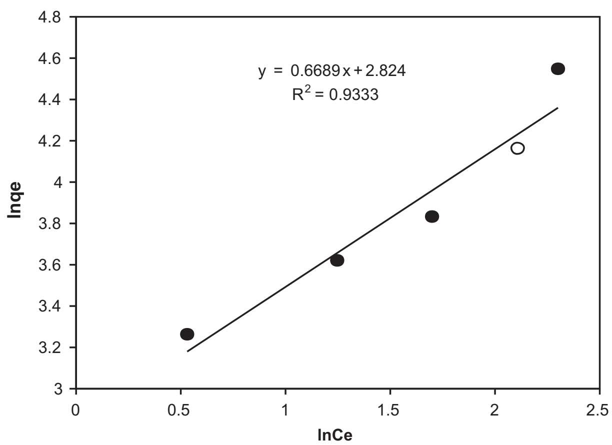

Fig. 2. Freundlich isotherms for the sorption of nitrate onto banana peels. Initial concentration of nitrate: 14.7 ppm; initial pH: 7.34; temperature: 25˚C.

The Langmuir and Freundlich plots for the case of using fly ash adsorbent are shown in Figs. 3 and 4, respectively. The parameters for both models are listed in Table 2.

It can be said that both models can be used for representation of nitrate using adsorbents, banana peels and fly ash. But since the R^2 is an indication of goodness of fit and how the data favored the linear trials, it is clear (Table 2) that the data conform Freundlich model for the case of banana peels, while they

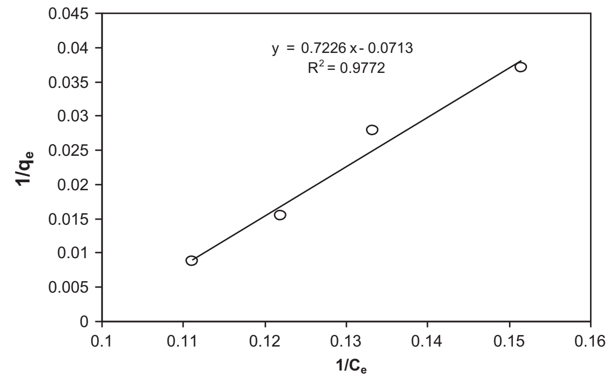

Fig. 3. Langmuir isotherm for the sorption of nitrate onto fly ash. Initial concentration of nitrate: 14.7 ppm; initial pH: 7.34; temperature: 25˚C.

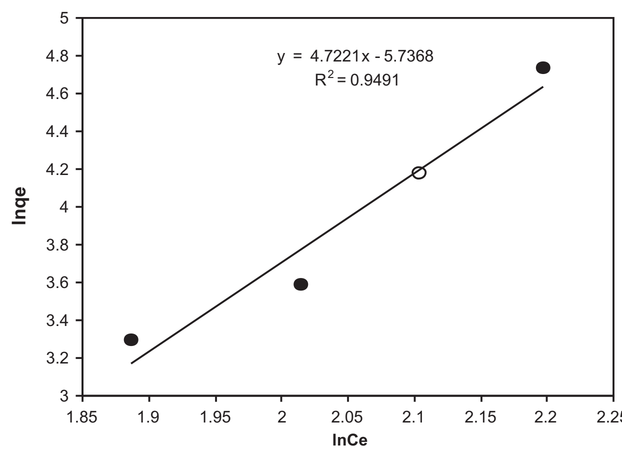

Fig. 4. Freundlich isotherm for the sorption of nitrate onto fly ash. Initial concentration of nitrate: 14.7 ppm; initial pH: 7.34; temperature: 25˚C.

conform Langmuir model for the case of fly ash adsorbent

According to Table 2, the values of $q_{\max}$ and K_L for banana peel are higher than those of fly ash. This means that the capacity of banana peel for nitrate attachment is higher than that of fly ash and the affinity, based on K_L value, of nitrate toward fly ash is greater than that of banana peel.

Table 2
Langmuir and Freundlich constants using fly ash and banana peel adsorbents

Adsorbents	Langmuir			Freundlich		
	K_L (L/mg)	$q_{\max}$ mg/g	R^2	$1/n$	$K_F\ [\frac{mg^{(1-\frac{1}{n})} l^{\frac{1}{n}}}{g}]$	R^2
Banana peel	0.1818	0.106	0.929	4.7221	17.15	0.9333
Fly ash	0.098	0.0142	0.9772	0.6689	3.225×10^{-3}	0.949

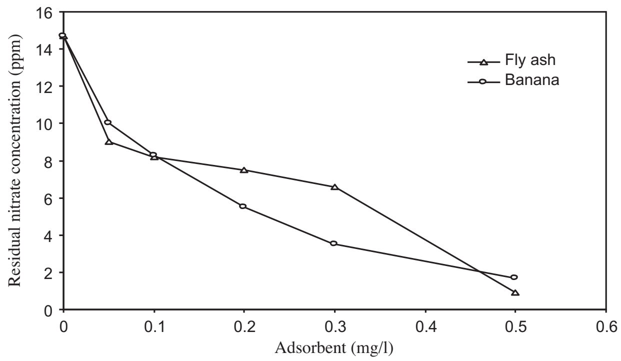

Fig. 5. Effect of adsorbent concentration on nitrate removal at 25˚C, pH = 7.4 with 14.7 initial concentration of nitrate.

4.1. Effect of adsorbent concentration on nitrate removal

The effect of adsorbents concentration on the nitrate removal process has been studied by adding different amounts of adsorbent to the solution. Adsorption was followed until the equilibrium and final residual nitrate concentration was recorded for each sorbate concentration. The results are shown in Fig. 5.

It is seen that nitrate removal increased with increasing amount of adsorbent. This is an expected trend which is due to the increase in the active sites available for adsorption. It was also noticed that the use of large amount of adsorbent, beyond 0.5 mg/l does not enhance removal process significantly. Generally, it can be said that removal efficiently of nitrate by fly ash is greater than that of banana peels particularly at high sorbent concentration.

4.2. Effect of contact time

The effect of contact time on the amount of nitrate adsorption. This is shown in Fig. 6 for both adsorbents. It is seen that residual nitrate concentration decreases with contact time. Nitrate concentration reaches constant value after 10 min, which mean that this adsorption process is relatively fast. The initial sharp drop in nitrate concentration is also an indication of the speed of the sorption process by the two adsorbents. The result of Fig. 6 also indicates that sorption of nitrate by fly ash is faster than that by banana peels. The quick removal of nitrate was also reported by Ozturk and Bektas [5] using sepiolite activated carbon.

4.3. Effect of temperature

The results for the effect of temperature on the adsorption of nitrate from waste water onto banana peels and fly ash are shown in Fig. 7. It is seen for both adsorbents that nitrate uptake increases with increase in temperature, an indication of endothermic nature for this sorption process.

The enhancement in adsorption capacity might be due to the possibility of increase in the number of active sites for the adsorption, with the increase in temperature .This may also be a result of an increase in the mobility of the nitrate molecules with the rise in temperature. The endothermic nature of sorption process was also obtained by [5] for nitrate removal from aqueous solution by activated carbon prepared from sugor bagasse. The result of 4.7 also indicates that nitrate uptake by fly ash is greater than that by banana peels for all temperature.

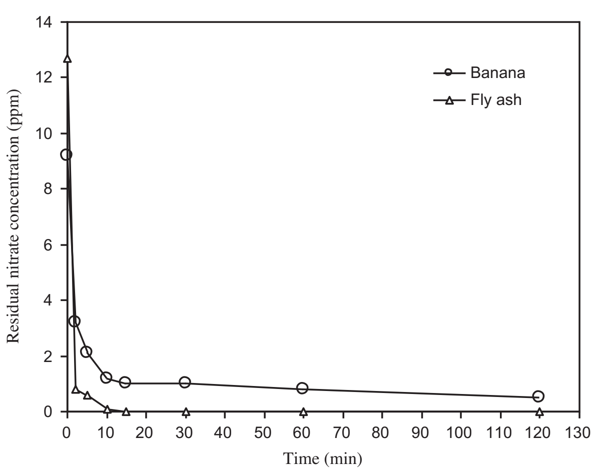

Fig. 6. Effect of contact time on the adsorption of nitrate onto fly ash and banana peels using 18 ppm initial nitrate concentration at pH 7.4 and 25˚C.

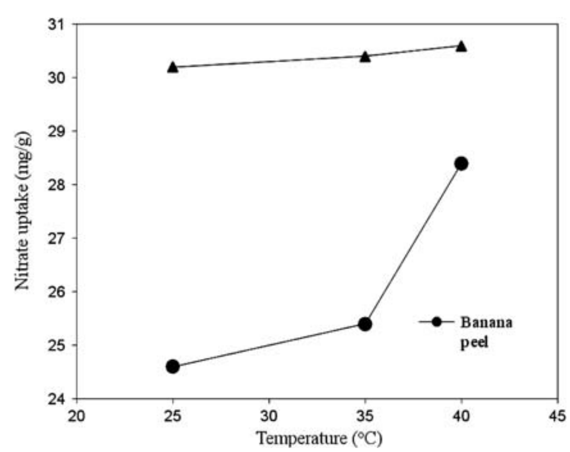

Fig. 7. Effect of temperature on the adsorption of nitrate by fly ash and banana peels using 18 ppm initial nitrate concentration at pH 4.7.

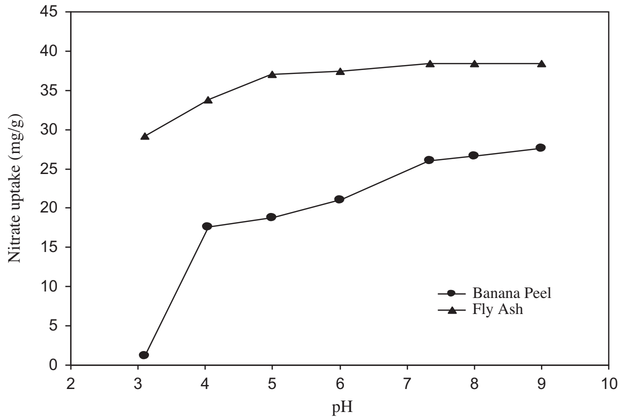

Fig. 8. Effect of pH on the adsorption of nitrate by fly ash and banana peels using 18 ppm initial nitrate concentration at 25℃.

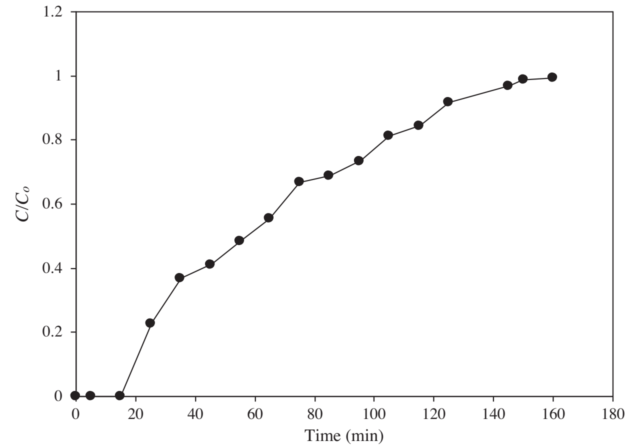

Fig. 9. Breakthrough curve for the banana peel in adsorption column.

4.4. Effect of pH

The removal of different compounds from the aqueous solutions by adsorption is highly dependent on pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The effect of pH on removal of nitrate for both adsorbents was investigated; results are given in Fig. 8.

An increase in nitrate uptake for both adsorbents with increasing suspension pH is observed. The removal efficiency increased by raising the pH from 3 to 8 and reaching maximum value at pH 8, and then it remains constant at 9. It is seen that the amount of adsorbed nitrate by fly ash is much higher than that of banana peel for all pH values. This can be explained by the fact that the chemical constituents of fly ash such as CaO and Al_2O_3 are playing an important role in chemical coagulation besides adsorption. These results are in good agreement with previous studies for sorption of ammonium by fly ash (Ugurlu and Karaoglu, [8]).

The result of Fig. 8 also prevail that nitrate uptake by banana peels is very low at low pH and significantly enhance by pH augmentation This could be due to active sites on the surface of banana peel that are responsible for sorption process, and these may become accessible at higher pH values.

4.5. Continuous adsorption process

As an attempt to implement this sorption into reality, the sorption process was carried out using glass packed-column constructed in the workshop. A 50 g of banana peel was packed in the column and wastewater was continually pumped to one end of the column at a rate of 600 ml/min with nitrate concentration of 18 ppm. Over different periods of time, samples were collected from the other end of the column and were analyzed for their nitrate content. The process was continued until the concentration of the effluent of the column becomes the same as that of the inlet. The results are shown in Fig. 9. It is seen that breakthrough occurred after 15 min and steady state is achieved after 160 min. This is an indication of column saturation. Such result indicates that it is possible to use this sorption process for real wastewater treatment plant.

4.6. Mechanisms of adsorption

Prasad and Srivastava [9] studied sorption of phosphate by fly ash. They attributed phosphate attachment on fly ash to ion exchange, chemical, or physical adsorption and precipitation mechanism. Since fly ash constituents are mainly metal ions, it can be said that also nitrate attachment to the surface of fly ash could also be due to ion exchange mechanism.

The work of Allen et al. [10] on sorption of heavy metals using banana peels demonstrated that sorption by banana peel attributed to ion-exchange; they reported that the main mechanism responsible for metal sequestering is ion exchange. They also reported that carboxylic groups R–COO$^-$ of banana peel constituents are the most probable sorption sites. Thus, it is possible that sorption of nitrate by banana peel used in this work is also attributed to carboxyl group and complexation is the possible mechanism. This could not be verified in this project due to lack of equipment for further analyses.

5. Conclusions

Based on the result presented, the following conclusions remarks can be drawn:

(1) According to sorption isotherm measurements, since fly ash follows Langmuir isotherm that adsorption of nitrate onto fly ash take place at homogeneous sites, i.e. all the adsorption sites are equal.
(2) Adsorption of nitrate onto banana peels is heterogeneous systems since it more likely follows Freundlich isotherm.
(3) Generally fly ash is a better adsorbent than banana peels as sorption of nitrate is more favorable.
(4) Treatment of waste water by adsorption onto fly ash and banana peels increase with increasing the dosage of these adsorbents.
(5) Adsorption process in this study is an endothermic process since increasing temperature resulted in an increase in nitrate uptake.
(6) Treatment of water by adsorption depends on the value of pH, as the experiments showed that an increase in removal of nitrate by both adsorbents with the increase in the pH of the solution.
(7) It is possible to remove nitrate using banana peel backed column, while it was difficult to operate the column using fly ash due to mud-like formation such that there was not flow.

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