



REMOVAL OF THE NITRATE FROM AQUEOUS SOLUTIONS USING POWDERED PEEL OF *CITRUS RETICULATE* FRUITS

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ABSTRACT

Aqueous nitrate solutions containing 10,20,30,40 and 50 ppm of nitrate were prepared. These solutions were subjected to batch type experiments to find out the effect of agitation time on the removal of nitrate using powdered peel of *Citrus reticulata*. The results were haphazard. Further, the effect of time on the removal of nitrate was found out by more addition of 200 mg of powdered peel of *Citrus reticulata* to 10, 20, 30, 40 and 50 ppm of aqueous nitrate solution. The studies predicted the absence of adsorption mechanism and the removal have not obeyed Freundlich adsorption isotherm. The removal mechanism may be the reduction process and the *Citrus reticulata* powder is expected to possess antioxidant property.

INTRODUCTION

Water is an important substance required for existence of all life. It is present in various resources such as rivers, lakes and streams etc. (Rangwala 1997). Any human activity that impairs the quality of water for various uses may be called water pollution. With exploding population and increasing industrialization and urbanization, water pollution by agricultural, municipal and industrial sources has become a major concern for the welfare of mankind (Dara 2002). These sources release various heavy metals and salts including nitrates into the water. According to WHO, the permissible level of nitrate in drinking water is 45 mg/L (Abbasi 1998).

Synthetic fertilizer wastes contain enormous quantities of nitrates. The nitrates are also the end products of aerobic stabilization of organic nitrogen (Manivasakam 1997). Main sources of nitrate in waters are from the atmosphere, sewage, industrial effluents, agriculture and run-off. Nitrogen wastes also increase BOD and COD. Nitrate poisoning in infant animals including humans can cause serious health problem and even death. The lower acidity in an infant's intestinal tract permits the growth of nitrate reducing bacteria that convert the nitrate to nitrite, which is then absorbed into the blood stream. These nitrites react with secondary amines present in food and form carcinogenic nitric compounds. Nitrite has a greater affinity for haemoglobin than oxygen and thus replace the oxygen in the blood complex. The body is denied of the essential oxygen, and in extreme cases the may victim suffocate. Because of oxygen starvation a bluish discolouration of the body occurs. Nitrate poisoning has been referred to as the blue baby syndrome or methaemoglobinaemia. Nitrate poisoning is also known to cause gastrointestinal troubles, nausea, vomiting and headache (Howard & Donald 1985). Hence, an attempt was made for the removal of nitrate from aqueous solutions using natural products.

MATERIALS AND METHODS

Nitrate was estimated by brucine sulphate method (Manivasakam 1997). For the removal of nitrates from aqueous solutions a low cost material namely the peel of *Citrus reticulata* (orange) was used.

The orange peel was shade dried, powdered and then sieved through ASTM No. 250 and was stored in an air tight container.

For finding out effect of agitation time on nitrate removal, a series of flasks containing 100 mL of 10, 20, 30, 40 and 50 ppm of aqueous nitrate solutions were prepared. 200 mg of the powdered peel of *Citrus reticulata* was added and agitated for 3 hrs. Samples were collected once during half an hour and the percentage of nitrate removal was estimated. Another series of the same flasks was kept for 12 hrs and nitrate was detected at the end for finding out effect of time on removal of nitrate.

Langmuir Isotherms

The modified Langmuir equation is written as,

$$C_e/q_e = (1/Q^\circ b) + (C_e/Q^\circ)$$

Where, C_e = equilibrium concentration of nitrate (mg/L)

q_e = amount of nitrate adsorbed at equilibrium (mg/g)

Q° and b are Langmuir constants

Q° = is a measure of capacity of adsorbent (mg/g)

b = is a measure of energy of adsorbent

The values of Q° and b are determined from the slope and intercept of the curve obtained by plotting C_e/q_e vs C_e .

A linear plot confirms the applicability of Langmuir isotherm.

Freundlich Adsorption Isotherms

The 'isotherm has been proposed by Freundlich for dilute and moderately dilute solutions. It is represented empirically by the expression:

$$q_e = kC_e^{1/n}$$

q_e = amount of nitrate adsorbed at equilibrium (mg/g)

C_e = equilibrium concentration of nitrate (mg/L)

The modified equation is:

$$\log q_e = \log k_f + 1/n \log C_e$$

The values of $1/n$ and k_f are determined from the slope and intercept of the curves by plotting $\log q_e$ vs $\log C_e$, where k_f is the measure of sorption capacity (mg/g) and $1/n$ is the measure of sorption intensity (Vaishya & Prasad 1991). The linear plot confirms the applicability of Freundlich isotherm.

RESULTS AND DISCUSSION

The results of the removal of nitrate at various shaking time intervals are given in Table 1 and Fig. 1, and the effect of total time on removal of nitrate in Table 2. About 48% of nitrate removal has been noticed from 10 ppm aqueous nitrate solution after 30 min and about 20% removal was found after 120 min. Further, with aqueous nitrate solution, 60% nitrate removal was noticed after about 90-150 minutes. This confirms the absence of adsorption. The values obtained following the agitation of aqueous nitrate solution with low cost material do not show regular increase thereby confirming that the removal was not adsorption, as adsorption follows a regular pattern with time.

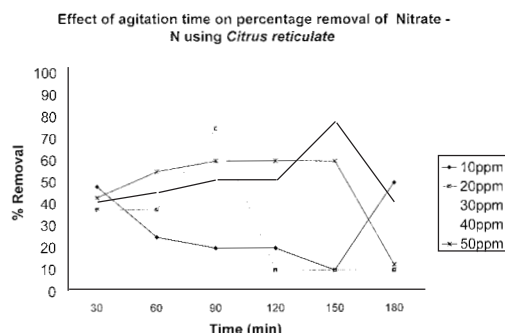


Fig. 1: Effect of agitation time on percentage removal of nitrate-N using *Citrus reticulata*.

Though many standards permit about 45 mg/L of nitrate, concentration above 10 mg/L of nitrate is said to cause health problems (Burt et al. 1993, Kvasnicka & Krysl 1990) due to ingestion of nitrate into stomach followed by its reduction to nitrite.

Even the nitrate concentration of 19-29 mg/L in well waters has resulted in spontaneous abortions within first 8 to 11 weeks of pregnancy in USA (Centre for Disease Control and Prevention 1993). The same centre found that when the ladies were shifted to use nitrate free drinking water they have delivered healthy babies. Hence, this study urges the removal of nitrate in a cost effective manner. The haphazard nature of percentage removal values suggest that the mechanism existing is not adsorption, as the values could not be fit in Freundlich isotherms.

Irrespective of the initial nitrate concentration, the percentage removal was estimated to be 100 after a time interval of 12 hrs.

It is a well known phenomenon that microbial denitrification takes place in environment (Ruby 2004). Though various other processes exist for the removal of nitrate such as reverse osmosis and electrodialysis, these processes were found to result in problems of disposing the concentrate ob-

Table 1: Percentage reduction of nitrate at various time intervals using shaking technology.

Sl.No	Agitation Time (min)	Concentration of NO ₃ ⁻ (ppm)				
		10	20	30	40	50
1	30	48	37.5	30	40	43
2	60	25	37.5	50	44	55
3	90	20	75	83	50	60
4	120	20	10	33	50	60
5	150	10	10	78	77	60
6	180	50	10	-	40	12.5

Table 2: Effect of time on percentage removal of nitrate.

S.No	Concentration (ppm)	% Reduction of Nitrate
1.	10	100
2.	20	100
3.	30	100
4.	40	100
5.	50	100

tained as well as they are costlier too.

As an alternative, the use of *Pseudomonas*, *Alkaligenes* and *Flavobacterium* for the biological denitrification has been made, but these processes need other treatments such as filtration and disinfection to be followed. Nitrate removal using filter beds comprising of soil and aquatic plants has also been tried.

Comparatively, the present study confirms the suitability of utilization of the powdered peel of *Citrus reticulata* for the nitrate removal, which does not pose any health hazard later. Disinfection alone could provide potable water. The mechanism may be the reduction of nitrate, but further studies could confirm the exact mechanism.

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