Sorption of Nitrate Salts from Wastewater without and with Modification Orange Peel

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Abstract

This investigation deals with the use of orange peel (OP) waste as adsorbent for removal of nitrate (NO_3) from simulated wastewater. Orange peel prepared in two conditions dried at 60C° (OPD) and burning at 500 °C (OPB). The effect of pH: 2-10, contact time: 30- 180 min, sorbent weight: 0.5- 3.0 g were considered. The optimal pH value for NO_3 adsorption was found to be 2.0 for both adsorbents. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Freundlich model was found to fit the equilibrium data very well with high-correlation coefficient (R^2). The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation ($R^2 > 0.95$ and 0.94) for the orange peel adsorbent at 500 °C (OPB) and at 60 °C (OPD), respectively. The results showed that the orange peel was found to be an attractive low cost adsorbent for the treatment of wastewater.

Keywords: Orange peel (OP); Nitrate; Sorption; Isotherms; Kinetics; Wastewater.

Introduction

Nitrate contamination in surface and ground water has become an increasingly important problem for all over the world. Although nitrate is found in moderate concentrations in most of the natural waters, higher levels in ground water mainly result from human and animal waste, and excessive use of chemical fertilizers. The other most common sources of nitrate are uncontrolled land discharges of municipal and industrial waste waters, overflowing septic tanks, processed food, dairy and meat products, and decomposition of Decaying organic matters buried in the ground [1,2]. The high concentration of nitrate in drinking water leads to the formation of nitrosoamine, which is related to cancer and increases the risk of diseases such as methanoglobinemia in newborn infants [3,4]. Nitrate is more toxic than nitrite and can cause human health problems such as liver damage and even cancers. Nitrate can also bind with hemoglobin and create a situation of oxygen deficiency in infant's body called methemoglobinemia. Nitrite, however, can react with amines chemically or enzymatically to form nitrosamines that are very strong carcinogens [5].

For removal nitrate from wastewater, adsorption has become one of the most economic and effective method. The process is superior to many other methods of water reuse by virtue of its low initial cost, low energy requirements, simplicity of design and

possibility of reusing the spent carbon via regeneration [9]. Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. In the past, the adsorption process has not yet been used extensively in wastewater purification but demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process of adsorption on adsorbents. Adsorbent is a very expensive adsorbent for the removal of pollutant so other inexpensive adsorbents must be investigated [10,11].

In recent years, agricultural by-products have been widely studied for NO_3 salts removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, pomegranate rind and compost and leaves [6]. The use of orange peel as a biosorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. As a low cost, orange peel is an attractive and inexpensive option for the biosorption removal of dissolved metals. Ajmal et al. employed orange peel for metal ions removal from simulated wastewater [7,8].

Therefore, the present study was undertaken to produce adsorbent by thermal and physical activation process utilizing orange pe as abundant local raw material for application in efficient nitrate removal. The effects of various operating conditions, namely, pH of solution, initial concentration of anions, contact time, and temperature, were investigated. used sulfur and limestone for nitrate removal from potable water in a batch study.

Materials and Methods

1. Sorbent Preparation

Orange peel adsorbent (OP adsorbent) was collected from a local juice manufacturing industry. OP was cut into small pieces, dried in an oven at 60 °C for 24 h and crushed. The powdered orange peel was washed with hot water and dried in an oven at 60 (OPD) and burning in the furnace at 500 °C for 12 h (OPB). After drying they were sieved to particle size 0.5 mm, and used as an adsorbent.

2. Chemicals

NO_3 solutions were prepared by diluting 1000 ppm of KNO_3 Potassium Nitrate (Scharlau (30 % wt/wt)) stock solution with demonized water to a desired concentration range between 25 and 200 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with diluted and concentrated HCL and NaOH solutions, respectively. Insignificant decreases in the final equilibrium pH were recorded, so during the uptake pH was assumed constant.

3. Adsorption Procedure

Batch adsorption experiments were carried out by agitating 1 g of the orange peel with 100 ml of NO3 solutions of desired concentrations and pH at room temperature using an orbital shaker operating at 200 rpm. The effect of pH was studied by adjusting the pH of the solutions using (1N) HCL or (1N) NaOH solution.

The effect of initial salts concentrations was carried out by shaking 100 ml NO_3 solutions of desired concentrations (25, 50, 75, 100, 150 and 200 mg L^{-1}) with 1 g of the adsorbent. All the samples were adjusted to the optimum pH prior to the addition of the adsorbent. The

samples were withdrawn from the shaker at pre-determined time intervals and NO₃ solution was separated from the adsorbent by centrifugation at 4000 rpm for 20 min. Blank runs, with only the adsorbents in 100 ml of double-distilled water, were conducted simultaneously at similar conditions to account for any color leached by the adsorbents and adsorbed by glass containers.

All the investigations were carried out in duplicate to avoid any discrepancy in experimental results and salts solution controls were kept throughout the experiment to maintain quality control. The percentage of salts adsorption by the adsorbents was computed using the equation [2]:

$$\text{Removal eff. (\%)} = \frac{c_i - c_e}{c_i} \times 100 \qquad \ldots(1)$$

Where,
c_i = initial NO₃ concentration in sample (mg/L)
c_e = equilibrium NO₃ concentration in sample (mg/L).

Result and Discussion

1. Characteristics of the Adsorbents
The chemical structure of this orange peel adsorbent is shown in Table 1.

Table 1: Chemical composition of the (OP) by X-ray fluorescence analysis

Characteristic	Values
CaO	1.43%
K2O	0.17%
SO3	0.15%
MgO	0.11%
Fe2O3	0.12%
SiO2	0.09%
P2O5	0.06%
BaO	0.01%
SrO	0.02%
Al2O3	0.02%
NiO	0.01%
Organic matter	97.83%

2. Effect of pH
The effect of pH on removal efficiency of nitrate by OP is shown in Figure 1. The removal efficiency of OP prepared at 60 °C (OPD) and OP burned at 500 °C (OPB) was decreased from 90 to 20 % and 95 to 71 %, respectively, when the initial pH of the aqueous solution was increased from pH 2 to 10. The nitrate content was decrease in the pH range of 2–6. However, removal efficiency for both OP adsorbents was increased to 88% for OPD and 95% for OPB adsorbent, when the pH remained constant at pH 2. Though there is increase in OH⁻ concentration at increased pH, yet removal efficiency of NO₃ decrease. This may probably due to the preferential adsorption of Nitrate. Among OH⁻ and NO₃, affinity of OP adsorbent 500 °C for NO₃ is greater than (OH⁻) [13].
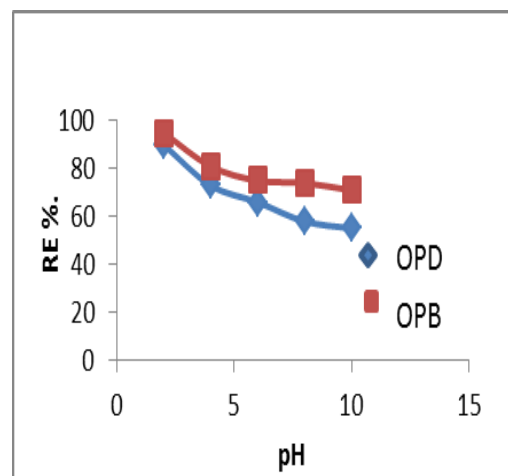

Fig. 1: Removal of NO₃ by OPD and OPB at dosage 1% (W/V), initial concentration 50 mg/L, temp. 25 °C, pH 2, agitation speed 200 rpm and contact time 3 h

3. Fourier-Transform Infrared Analysis (FTIR)
Infrared spectra of Orange peel (OP) samples before and after nitrate ions binding were examined using (Shimadzu FTIR 8000 series spectrophotometer). The functional groups have been identified in Figure 2 (a-c). As seen in these figures the

spectrum pattern of loaded OP showed changes in the peak absorption as compared to unloaded OP which result from adsorption process. Contribution of each functional group in this process is summarized in Tables 2 and 3.
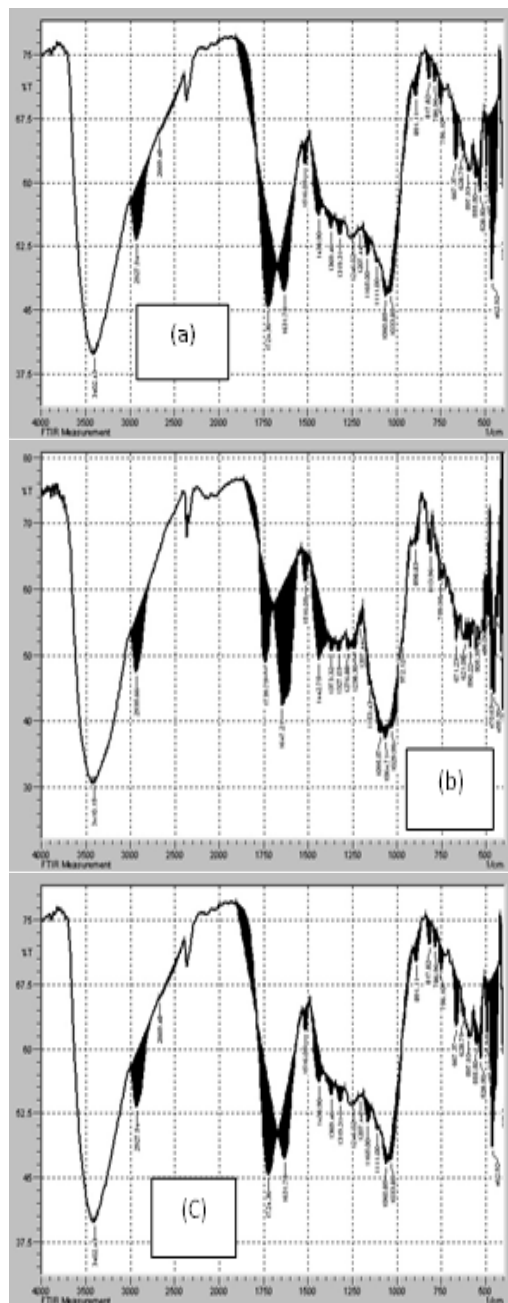

Fig. 2: Functional groups (a) before OP loaded without NO_3 salts (b) after OPD loaded with NO_3 salts (C) after OPB loaded with NO_3 salts

Table 2: FTIR functional groups for OPD

Wave number (cm^{-1})	Assignment Groups	After adsorption of NO_3
3398.57	Carboxylic acid, Amides	3402.43
1627.92	Amines, Alkenes	1631.78
1435.04	Carboxylic acid, Alkenes	1438.90
1161.15	Ketones, Amines, Alkyl halides	1165.00
725.23	Alkyl halides, Aromatic	756.10
609.51	Alkyl halides, Alkyanes	628.79
586.36	Alkyl halides	597.93

Table 3: FTIR functional groups for OPB

Wave number (cm^{-1})	Assignment Groups	After adsorption of NO_3
3398.57	Carboxylic acid, Amides	3410.15
2927.94	Carboxylic acid, Alkanes	2935.66
1033.85	Carboxylic acid	1064.71
894.97	Alkenes	898.83
756.10	Aromatic	759.95
667.37	Aromatic	671.23
559.36	Alkyl halides	590.22

4. Effect of Sorbent Dose

The sorbent amount is one of the important parameters used to obtain the quantities uptake of NO_3 salt .The sorbent amount was studied by varying the quantity of OP adsorbent (0.5, 1, 1.5, 2, 2.5, 3) g in 100 mL of 50 mg/L of NO_3 solution. Sorption of NO_3 was increased as the sorbent amount increased. The results were expected because for a fixed initial NO_3 concentration, increasing adsorbent amount provides greater surface area or sorption site, this result agreement with those obtained by other researchers [12]. The higher removal efficiency was achieved by using 2 g/100 ml sorbent dosages. The removal efficiency of OPD adsorbent and OPB adsorbent was increase from 89 to 97%

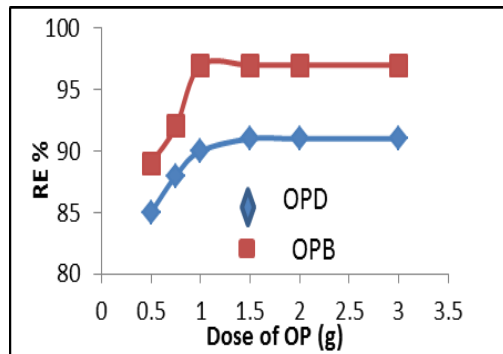and 85 to 91%, respectively, as show in Figure 3.

Fig. 3: Removal of nitrate by OPD and OPB with different contact time, initial concentration 50 mg/L, adsorbent dosage: 2% w/v temperature 25°C, pH= 2; agitation 200 rpm

5. Effect of Contact Time

The effect of contact time on the removal of nitrate by OPD and OPB was observed to increase as contact time increased as shown in Figure 4 The concentration of nitrate using ODB was decreased substantially from initial concentration of 50–17mg/L within 1h of treatment where the removal efficiency was around 66% . For OP adsorbent, the percentage removal during the first hour was 58% , the initial concentration of 50mg/L was decreased to 21 mg/L. The final concentration of nitrate adsorbed by both samples reached equilibrium point within 2h of operation.
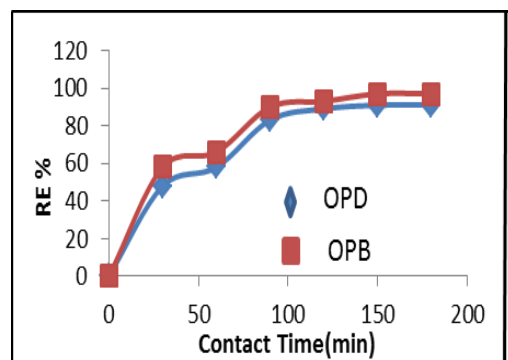

Fig. 4: Removal of nitrate by OP adsorbents with different contact time, initial concentration 50 mg/L, adsorbent dosage: 2% w/v temperature 25°C, pH= 2; agitation 200 rpm and pH= 2

6. Adsorption Isotherms

In order to find an equation which suitable for the results and can be used for design purposes; Langmuir and Freundlich isotherm equations have been used for the equilibrium modeling of adsorption systems. The form of Langmuir (linear form) is:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad \ldots(2)$$

Where C_e is the equilibrium concentration of the metal in solution (mg/L), q_e is the amount absorbed at equilibrium (mg/g), Q_o (mg/g) and K (L/mg) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_o) represents monolayer coverage of sorbent with sorbate and b represents the enthalpy of sorption and should vary with temperature. A linear plot was obtained when Ce/qe was plotted against Ce over the entire concentration range of metal ions investigated.

The Freundlich adsorption form (linear form) is:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \ldots(3)$$

Where q_e is the amount of metal ion adsorbed at equilibrium per gram of adsorbent (mg/g), Ce is the equilibrium concentration of metal ion in the solution (mg/L), k_f and n are the Freundlich model constants [13]. Freundlich parameters, k_f and n, were determined by plotting log q_e versus log Ce. The Langmuir and Freundlich adsorption isotherms of nitrate ions are given in Figures 5, 6 and Table 4.
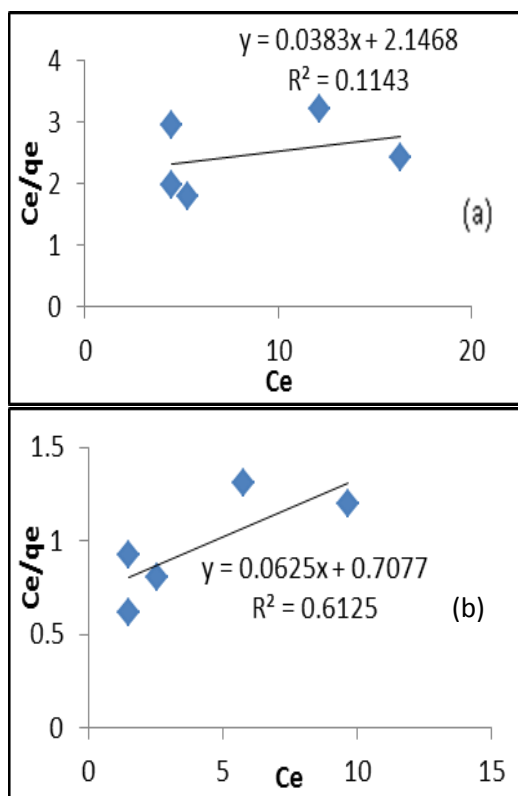
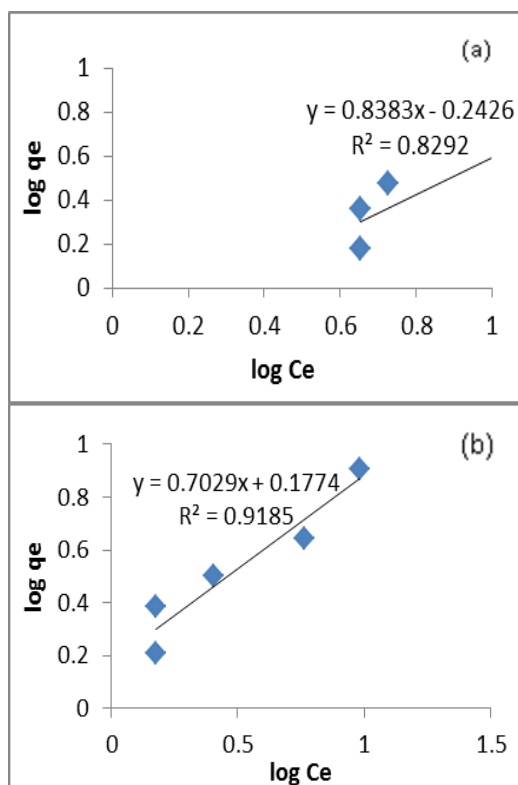Fig. 5: Langmuir plots of NO_3 sorption on (a) OPD (b) OPB

Fig. 6: Freundlich plot of NO_3 sorption on (a) OPD (b) OPB

Table 4: Langmuir and Freundlich constants for adsorption of NO_3 onto OP

Adsorbent	Isotherm Models		
	Langmuir		
	R²	a	b
OPD	0.114	26.31579	0.017707
OPB	0.612	16.12903	0.087694
	Freundlich		
Adsorbent	R²	1/n	K
OPD	0.829	0.838	0.572796
OPB	0.918	0.702	1.503142

These results showed that in both case (OPD or OPB) the best model is Freundlich.

7. Kinetic Modeling

Two kinetic models namely pseudo-first-order, and pseudo-second-order models have been discussed to identify the rate and kinetics of adsorption of nitrate on prepared orange peel adsorbent. The linear form of pseudo-first-order (Lagergren rate equation) equation is given in Eq. 4 [14]:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \qquad …(4)$$

And the linear pseudo-second-order model is given as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \qquad …(5)$$

Where q_{eq} is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k_1; k_2 is the equilibrium rate constant of pseudo first sorption (1/min).

Figure 7 (a, b) show a plot of pseudo-first and second-order kinetic model of nitrate adsorption on prepared adsorbent (for unmodified and modified), compiled in Table 3 along with correlation coefficient (R^2) values. It is seen from Table 5 that the theoretical q_e (cal) values calculated from the pseudo-first-order model did

not give reasonable values with regard to the experimental uptake ones, q_e (exp). Further, the correlation coefficient (R^2) is less than 0.99 suggesting that the present adsorption system does not follow pseudo-first-order process (in both case), while pseudo-second-order model is the best to describe our study.

Table 5: Comparison of sorption rate constants, experimental and calculated q_e values for the pseudo-first and second-order reaction kinetics for component systems

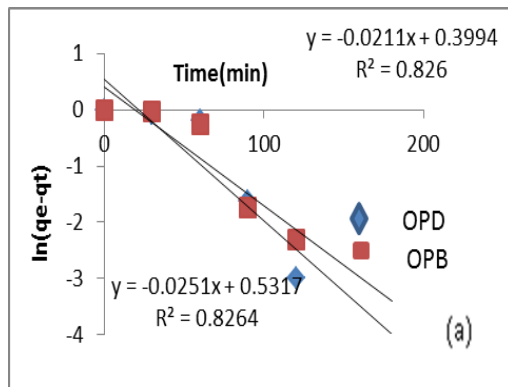| Adsorbent | Pseudo-first-order | | | |
	q_e exp. mg/g	k_1 1/min	q_e calculated mg/g	R^2
OPD	2.275	-0.025	1.8022	0.825
OPB	2.425	-0.021	1.4903	0.857
Adsorbent	Pseudo-second-order			
	k_2 g/mg.min		q_e calculated mg/g	R^2
OPD	0.01825			0.954
OPB	0.03185			0.972

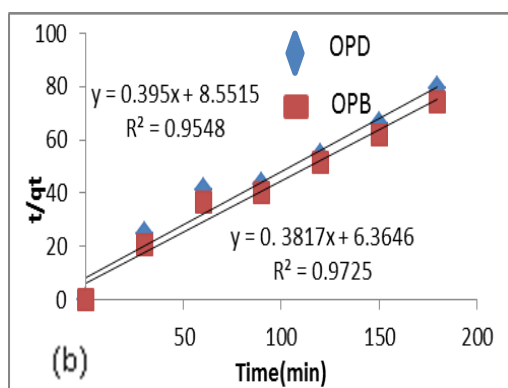Fig. 7a: Pseudo-first order kinetic for adsorption of NO_3 on OP

Fig. 7b: Pseudo-second order kinetic for adsorption of NO_3 onto OP

Conclusion

The results show that the adsorption of nitrate using orange peel occurred at wide range of concentrations. The time required for utilizing nitrate varies between 30-180 min depending on the initial concentration nitrate. The time of utilization increases as the initial concentration of nitrate increase.. The isotherm equilibrium studies confirmed that the Freundlich form and generalized models were the highest fitted models for the both adsorption process. Orange peel adsorbent which is dried at 500 °C was the best fitted than orange peel adsorbent which is dried at 60 °C. The maximum adsorption potential of orange peel adsorbent for NO_3 salts removal was 2.532 mg/g. Pseudo-second-order reaction kinetic has provided a realistic description of removal of NO_3 salts with closer experimental and calculated values of uptake capacity. Also correlation coefficients are higher in pseudo-second-order kinetics.

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