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Nitrate Removal from Aqueous Solution by Orange Peels as an Adsorbent

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ABSTRACT: One of the best water treatment technologies around the world has been the adsorption process. In this process activated carbon was considered as universal adsorbent for the removal of diverse types of pollutants from water. Thus, the widespread use of commercial activated carbon became restrictive due to its exorbitant operation and maintenance cost. In the present research work, the authors used activated carbon that has been produced from orange peels by chemical activation technique with$ZnCl_2$ as activating agent.The scanning electron microscopy (SEM) images of the activated carbon have shown the higher cavities.By using the energy dispersed X-ray (EDX) analysis, carbon content in the modified orange peels sample was detected. The optimum conditions of sorption were found to beat sorbent dose of 0.3 g in 100 mlwithconcentration 50 mg/L of NO_3^- solution, contact time =720 minutes and pH = 3. Under the optimum conditions, the removal efficiency was 86.00%.The adsorption mechanisms were investigated with two simplified kinetic models, i.e., first and second-order, and intraparticle diffusion were tested. The correlation coefficient obtained for second order kinetic model is 0.9961 which indicatedits effectiveness in adsorption capacity.

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KEYWORDS: Nitrate, Groundwater, Orange peels, Activated Carbon, Zinc Chloride, SEM, EDX.

I. INTRODUCTION

The environment has been affected by one of the water pollutants nitrate (NO_3^-) causing serious problems to aquatic life and other living being even though nitrogen (N) is an essential element for all living matter. The nitrogen (N) element in natural waters exists in different oxidation states such as nitrate (NO_3^-), nitrite (NO_2^-) and Ammonium (NH_4^+) with oxidation states of +5, +3 and –3 respectively. Among these, NO_3^- and NO_2^- are of more concern because of potential toxicity to human health especially threat to infants, causing the condition known as methemoglobinemia, also called "blue baby syndrome". Nitrites combine with haemoglobin to form methemoglobin, which decreases the ability of the blood to carry oxygen. Adults and older children are less susceptible when compared with infants to nitrate toxicity.

High levels of nitrate may also cause other health problems, like cancer, stomatitis and teratogenic effects when consumed for longer duration [1]. The excess nitrate (or nitrite) in the blood can react with amino acids, forming cancer-causing compounds called nitrosamines – a report by medical research. An increased risk may exist for stomach and bladder cancer, thyroid cancer, and non-Hodgkin's Lymphoma from long term consumption of nitrate [2]. Other risks associated with high level of nitrate toxicity arechildhood-onset diabetes, miscarriage and problems related to breathing in children.High nitrate levels in drinking water leads to increase in still births with low weight, weight gain becomes slow and reduced vitality can occur in livestock [3].

The US Environmental Protection Agency (EPA) has set the maximum contamination level (MCL) 10 mg/L and mg/L for nitrate and nitrite as N respectivelydue to these possible adverse health effects [4]. The World Health Organization (WHO) has set a maximum acceptable nitrate concentration of 45 mg/L to limit the risk to human health from nitrate in drinking water.

II. Literature Review

Chlorophyll pigments and low molecular weight substances like limonene are present in the Orange peels. It also has cellulose, hemi-cellulose, and pectin substances in it. Pectin is poly α1-4-galacturronic acids with varying quantity of carboxylic acid residues. The orange peels' better features are it has hydroxyl, and carboxyl groups

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which are important sites for metal sorption [5]. Agro – industrial and municipal waste is attractive for preparation of low cost adsorbents for disposal and it might also contribute to environmental protection [6].

Chemically modified lignite granular activated carbon (LGAC) with $ZnCl_2$at 5 pH and optimum contact time resulted in the maximum adsorption capacity 4.4 mg/g of dosage of LGAC in a batch adsorption study for removal of nitrate from aqueous solution.The adsorption process exhibited anendothermic and spontaneous nature of adsorption in their thermodynamic studies.Adsorption studies on competitive ions found as $Cl^- > CO_3^{2-} > PO_4^{3-}$**[7].**

In the batch studies, it was observed that the chemically modified orange peels by using NaOH resulted in chromium (VI) removal at optimum 2 pH and 4 mg/L dosage. It was also observed that the adsorption increases with the increase of contact time, and the equilibrium time found to be 180 minutes at the optimum pH and dosage [8]. Batch studies found to have optimal efficiency 94.3% at contact time 90 minutes and 7 pH in the investigation on ionic rice husk structural characteristics and adsorption properties for nitrate removal. In the adsorption process studies, it was observed pseudo first order and second order kinetics effective in removal and the effect on different ions found the order as $CO_3^{2-} > Cl^- > PO_4^{3-} > SO_4^{2-}$ [9].

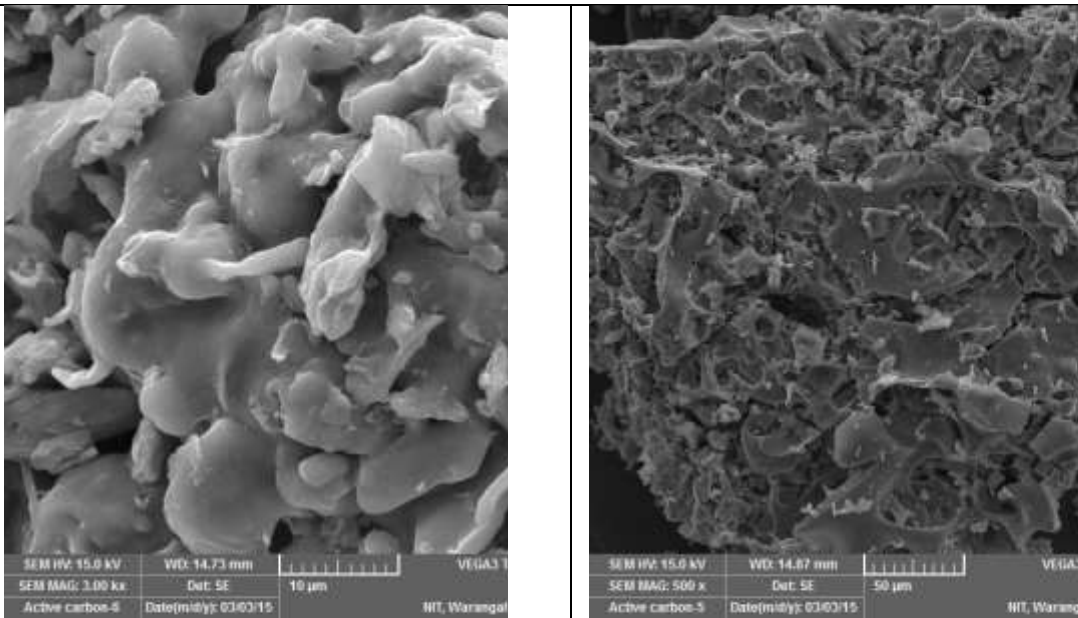
III. Materials and Methodology

3.1 Preparation of adsorbent and adsorbate solution

Activated Carbon has been prepared from the dried and grinded orange peels. Orange peels have been cut into small pieces and washed with tap water, then rinsed with de-ionized water and dried in the oven at 60º C for 24 hours until it reached a constant weight. Dried peels were ground and sieved through 75 µm sieve. It was preserved by keeping in the plastic-stopper bottles.The chemical activation of orange peels was done using $ZnCl_2$solution by adjusting pH with 0.1NH_2SO_4 and 0.1N HCl. The KNO_3 stock solution was prepared by dissolving KNO_3 in de-ionized water and then diluted to desire concentrationof nitrate in the aqueous solution for Nitrate removal studies.

The Activated Carbon (adsorbent) obtained at 600° C activation temperature; and its surface was modified with aqueous solutionof $ZnCl_2$ using chemical impregnation ratio of 1:1 i.e.10 g of activated carbon was treated with 10 g of $ZnCl_2$ in 100ml aqueous solution at 80º C for one hour under constant magnetic stirrer. Thenthe slurry was kept in oven at 110° C for 24 hours and then this was thermally activated for 1 hour in a muffle furnace at temperatures 400° C. The activated sample prepared in this way is cooled in desiccators and stored for adsorption studies.

The stored activated carbon further studied for its morphology using the scanning electron microscopy (SEM) technique.The SEM images shown in the figure 1 (a) and (b) are activated carbon resolution of 50 µm and 10 µm respectively.



(a) 50µm resolution	(b) 10 µm resolution

Figure1 (a) and (b). The SEM resolution images of activated carbon of 50 µm and 10 µm.

3.2 Adsorbent Dosage Effect

The activated carbon of varying quantity from 0.025 g to 0.8 g was placed into different conical flasks, and then

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100 ml of 50 mg/L concentrated nitrate aqueous solution with pH value 4 is poured into the each flask. Then the mixture is agitated for 1 hour at 30°C. The results obtained are shown in the figure 2. The % removal of nitrate varied from 14% for 0.025 g(0.25 g/L) dosage to 86% for 0.8 g(8.0 g/L) dosage. The optimum dosage is observed to be 0.3 g (3.0 g/L) as seen in the figure 2 where the removal efficiency is around 65%.

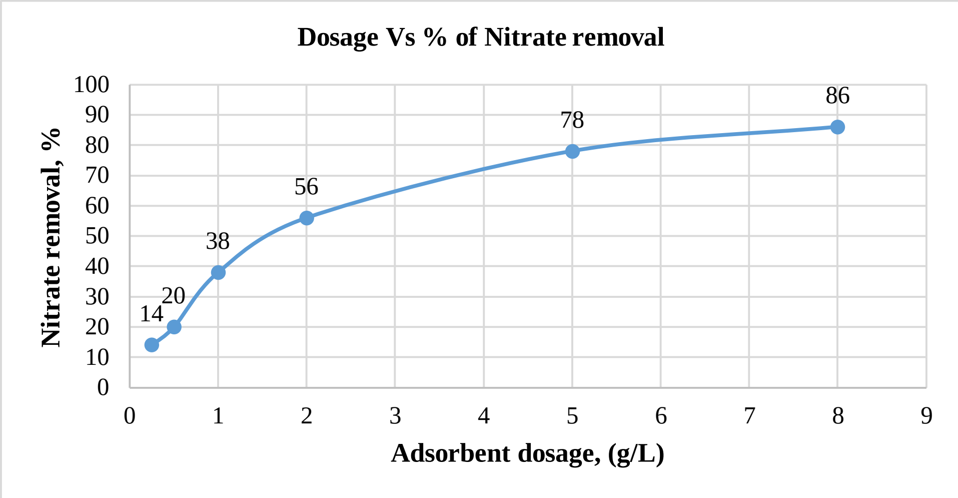

Figure 2.Plot between adsorbent dosage (g/L) and % of nitrate removal.

3.3Initial pH Effect

The experimental studies on initial pH effect were conducted on adsorption at pH range 2 to 8 at optimum dosage of 3.0 g/L. The pH was varied as desired, by adding sodium hydroxide and/or sulphuric acid solutions. Nitrate solution 100 mL with concentration of 50 mg/L added to adsorbent samples having 3.0 g/Leach. The mixtures are then shaken for 1 hour at 30°C. The optimum pH value observed to be 3 as seen in the figure 3 and the percentage of removal at that optimum pH is observed as 56%.

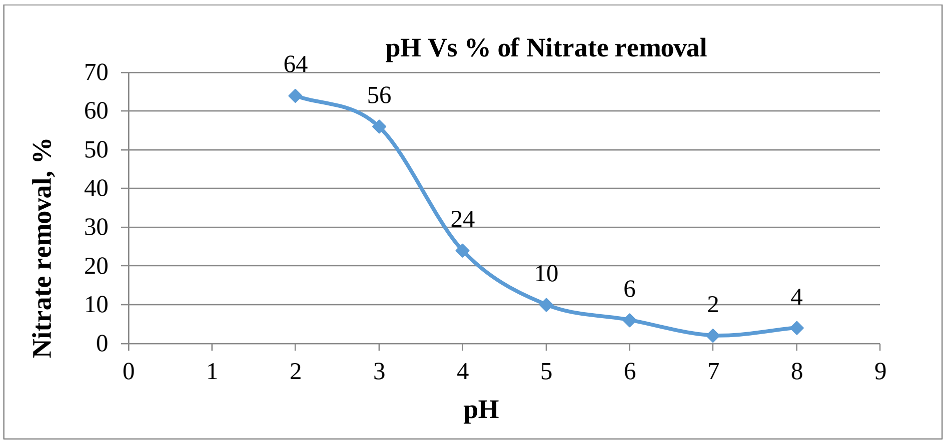

Figure 3. The graph between pH and % of nitrate removal.

3.4 Contact Time (Kinetic Study) Factor

In the contact time factor studies, nitrate aqueous solution 100 mLwith concentration of 50mg/L is added to adsorbent sample 3.0 g/Lwhich is optimum dosage and at optimum pH value 3. Then the mixture was agitated at 30ºC. The nitrate solution of each 100 ml kept in shaker for different contact timings15, 30, 60, 120, 240, 480, 720 and 1440 minutes. The observed nitrate removal in percentage at different timingsare plotted and shown in the figure 4. The maximum removal of about 88% is observed at the contact time of 720 minutes.

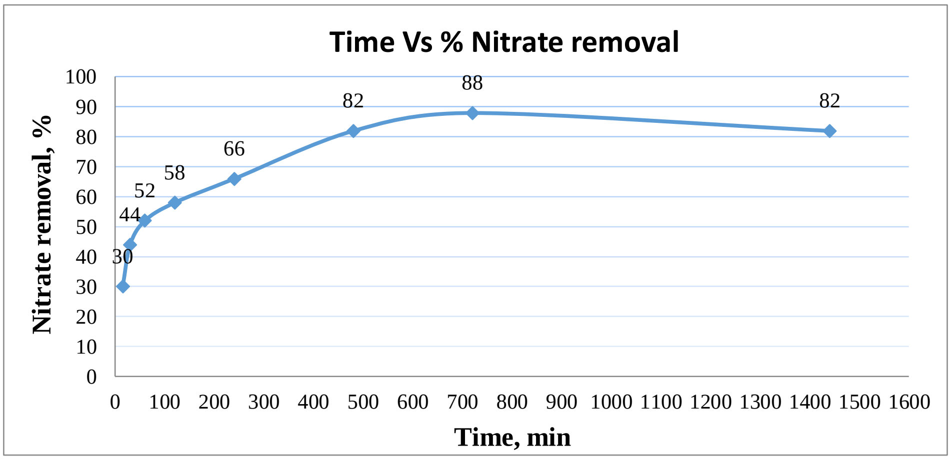

Figure 4. Plot between contact time (minutes) and % of nitrate removal

IV. Isotherms and Kinetic Studies

4.1Adsorption Isotherms

It is necessary to ascertain the most appropriate isotherm correlation for the equilibrium curve for optimizationof design of adsorption system; Adsorption isotherms illustrate the relation between adsorbent concentration and the accumulating capacity on the adsorbent surface at constant temperature. In this regard, the consistent experimental results with the two conventional isotherm models such as Langmuir and Freundlich isotherms were taken into account for this adsorption studies. The linear expression of Langmuir isotherm model is given in the equation (1).

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

Where, q_e (mg/g) is the amount of adsorbate per unit amount of adsorbent at complete monolayer coverage and 'b' (L/mg) is the Langmuir isotherm constant relating to the energy of adsorption and C_e is the concentration in mg. The values of Langmuir parameters, q_{max} and 'b' are obtained from the slope and intercept of the linear plots between $\frac{1}{q_e}$ and $\frac{1}{C_e}$.

The linear expression of Freundlich model is given in the equation (2).

$$\log (q_e) = n_F \log(C_e) + \log (K_f) \quad (2)$$

Where, K_f is the Freundlich constant with respect to the bonding energy, and n_F is the heterogeneity factor. The value of n_F varies with the heterogeneity of the adsorbent to the favorable adsorption process. The Freundlich isotherm constants $K_f$and $n_F$are obtained from the slope and the intercept of the plot between $\log(q_e)$ and $\log(C_e)$. In the Langmuir's model,another dimensionless parameter R_L isintroduced to indicate the favorability of adsorption and determined by $R_L=\frac{1}{1+bC_0}$. Where, C_o is the initial concentration of nitrate. The adsorption isotherm parameters which were calculated from the slope and intercept of the linear plots using the linearized form of the Langmuir and Freundlich together with the R^2 values are given in below figure 5 and 6 respectively. The adsorption isotherm parameters with obtained correlation are listed in the table 1.

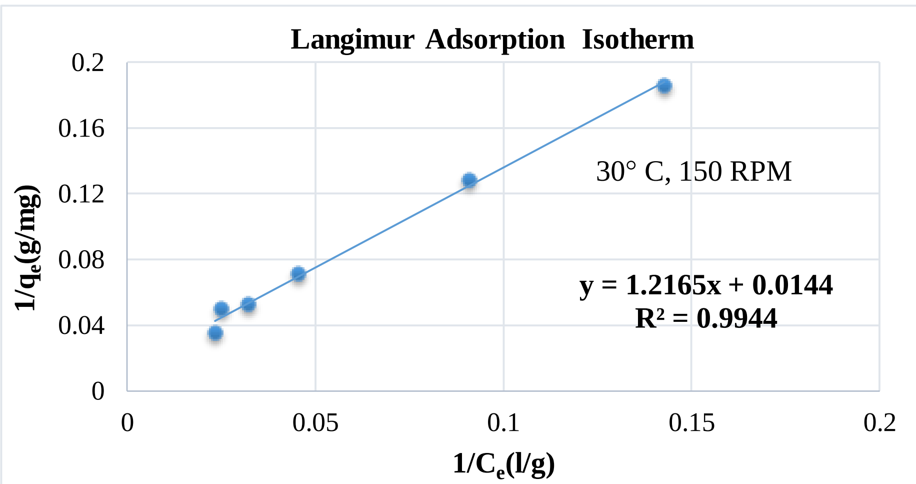

Figure5. Langmuir plot for nitrate adsorption onto activated carbon at 30°C and initial pH=3

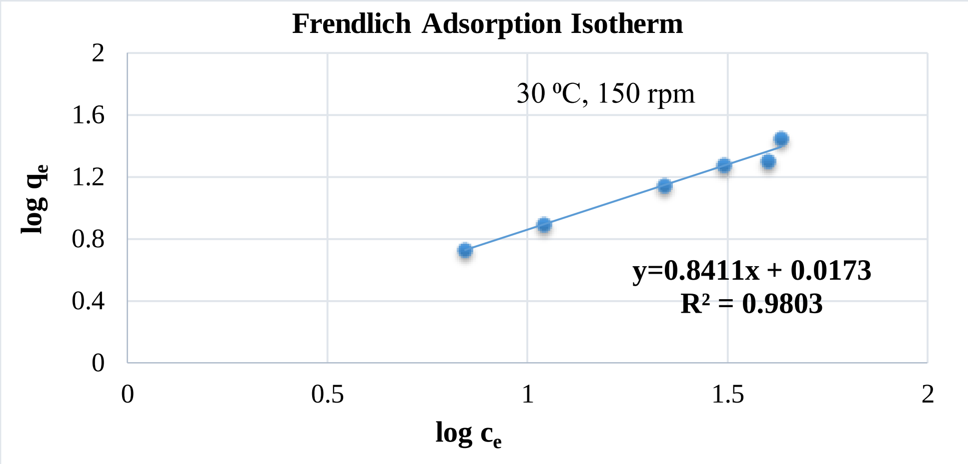

Figure 6.Freundlich Plot for Nitrate Adsorption onto Activated Carbon at 30°c and Initial pH=3

Table 1. Adsorption Isotherm Parameters

Isotherm	Langmuir parameters				Freundlich parameters		
Concentration of Adsorbate (NO_3^-)	q_{max} (mg/g)	b (L/mg)	R_L	R^2	K_f (mg/g)(l/mg)$^{1/n}$	n_F	R^2
50 mg/L	69.44	0.0118	0.628	0.9944	1.042	1.1889	0.9803

The Langmuir and Freundlich adsorption isotherm constants R_L and n_F are dependent on adsorption capacity and intensity respectively. The adsorption process is considered as beneficial when $n_F$and $R_L$values lie between 1 and 10, 0 and 1 respectively. In this case the obtained $n_F$and $R_L$valuesare1.1889 and 0.628. The correlation coefficients (R^2) values are 0.9944 and 0.9803 for Langmuir and Freundlich models respectively which indicate robustness of nitrate adsorption on the chemically modified activated carbon.

4.2 Adsorption kinetics

The adsorption mechanism depends upon the physical and/or chemical properties of the adsorbent and on the mass transfer process. In this study, the pseudo-first-order and the pseudo-second-order kinetic models were used to test the experimental datato find out the controlling mechanism of this adsorption process,.

Pseudo first-order and second-order models represent as given in the equations 3 and 4.

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \quad (4)$$

Where, q_e and q_t (mg/g) are the amounts of adsorbate per unit mass of Adsorbent at equilibrium and time t (min) respectively. Theequilibrium constants K_1 (min^{-1}) and K_2 (min^{-1}) are the pseudo first-order and second-order adsorption rate constants respectively.

In order to quantify the applicability of pseudo first order and second order models, linear plots of log (q_e-q_t) versus t and (t/q_t) versus t were used to check the best fit of the above models respectively. If any of these models is applicable, it should give a linear relationship, from which the parameters and their correlation coefficients (R^2) can be determined.In order to investigate the mechanism of nitrate adsorption process on activated carbon the pseudo first order and second order kinetic models were used to test the experimental data. The results obtained are shown in figures7 and 8 respectively.

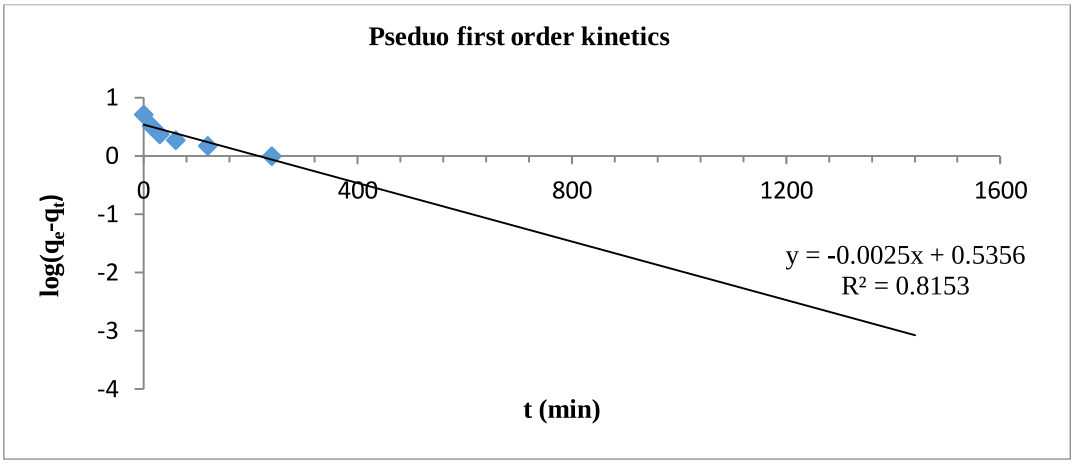

Figure7.Pseudo first order kinetics

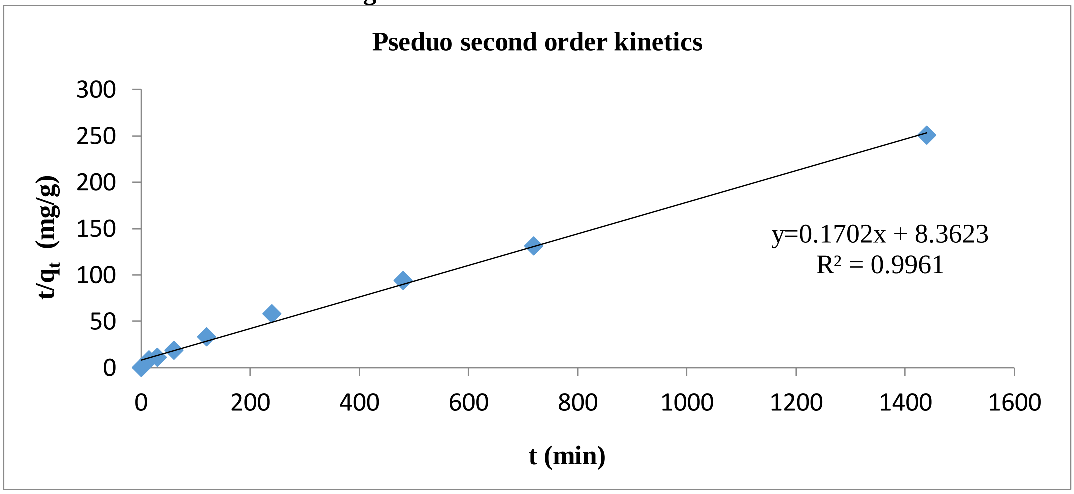

Figure8. Pseudo second order kinetics

The correlation coefficients and other constant parameters calculated for the Pseudo first and second order models are listed in the table2. The correlation coefficient (R^2) valuesof the pseudo first and secondorder models are 0.8153 and 0.9961 respectively which indicate suitability for adsorption process. However, when the q_e (exp) values are compared with q_e (cal) values for both first and second order, the second order correlation coefficient of q_e (cal) value is close to the q_e (exp) value, thus the pseudo second order kinetic model might be more suitable to describe the kineticsof adsorption processes of nitrate removal. This also suggests that during the adsorption of nitrate, there werechemisorptions between the adsorbate and surface of the adsorbent.

Table 2. Adsorption kinetic parameters

Concentration of adsorbate (mg/l)	q_e(exp) (mg/g)	Pseudo first order kinetics			Pseudo second order kinetics		
		K_1(min^{-1})	q_e (cal) (mg/g)	R^2	K_2(min^{-1})	q_e (cal) (mg/g)	R^2
50	4.925	0.00644	3.244	0.8153	0.003464	5.875	0.9961

V. Conclusions

On the basis of experimental and analytical calculations the following conclusions are drawn:

- The chemically modified activated carbon from orange peels with $ZnCl_2$is effective for nitrate removal.
- It is observed that around 65% of nitrate can be removed from 100 ml aqueous solution with 50 mg/L concentration of nitrate at optimum adsorbent dosage of 3g /L.
- Experimental study showed that nitrate adsorption increaseswith decrease in pH value of the solution.
- The results showed that optimum time for maximumnitrate adsorption is 720 minutes.
- The results showed that nitrate adsorption onto the activated carbon have robustness with the pseudo-second-order model.
- Equilibrium adsorption data for nitrate obtained for both isotherms are highly correlated. However, high

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correlation coefficient forthe Langmuir isotherm (0.9944) than the Freundlich isotherm (0.9803) exists. Since orange peel is a waste material, using it for thetreatment method seems to be economical.

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