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REMOVAL OF NITRATE FROM GROUND WATER USING ACTIVATED CARBON PREPARED FROM RICE HUSK AND SLUDGE OF PAPER INDUSTRY WASTEWATER TREATMENT

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ABSTRACT
Nitrate found in ground waters over the past decades has aroused serious concerns to associated administrators. Among different methods of removing nitrate, using adsorption technique has drawn attention due to its high efficiency as well as economic considerations. In this study, the effectiveness of activated carbon absorbents obtained from pyrolysis of rice husk on nitrate adsorption is explored, and the results of the adsorption by carbon prepared from primary sludge of wastewater treatment of paper industry have been compared. The results of experiments for both absorbers indicated that the maximum adsorption occurred in pH equal 4, as the system has reached equilibrium during 4 hour contact time. The maximum removal of nitrate for activated carbon obtained from rice husk was 93.5 (mg/gr), and for the sludge obtained from paper industry was 79.5 (mg/gr). The result of tests for both adsorbents suggests a direct relationship between the level of adsorption run by $Zncl_2$ used to activate adsorbents and the level of adsorbent. Moreover, the results of adsorption tests for adsorbents were adapted with Langmuir isotherm, and also the kinetics of adsorption was well fitted into pseudo-second-order model.

Keywords: nitrate, adsorption, activated carbon, rice husk, sludge, paper industry.

1. INTRODUCTION

Nitrate contamination in ground and drinking water caused concerns on a global scale. In the last decade, nitrate concentration has increased both in ground and surface water at a rapid rate. The increasing use of nitrogen fertilizers in agriculture sector is the reason for the contamination caused by nitrate. Other factors such as sewage, urban and agricultural runoffs, untreated wastewater disposal, industrial wastewater, septic system leachate, waste disposal site leachate, agricultural fertilizer, and nitrogen compounds added to the air through industry and cars also give rise to the pollutants in waters (Dong-Wan Cho *et al.* 2011). Due to its high solubility, nitrate is the most likely cause of the contamination in ground waters across the globe, and a potential threat to water resource, as well as increasing eutrophication (A.A. Hekmatzadeh *et al.* 2012).

Nitrate concentration increase in water would cause negative effects on human health: Blue baby Syndrome (Met Hemoglobin) especially in infants and the carcinogenic potential for nitrosamine (Sudipta Chatterjee *et al.* 2011). Recent studies indicated that increase in the amount of nitrate in drinking water would likely cause a variety of cancers in humans (P.C. Mishra *et al.* 2009).

Because of serious health problems associated with nitrate in drinking water, the Environmental Protection Agency (US EPA) has announced the maximum ensured nitrogen concentration to be 10 milligrams per liter in water (Amit Bhatnagar *et al.* 2010). So it is necessary to announce the concentration of the purified water nitrate to be below the permissible limit in order to supply water.

Due to its high solubility and sustainability, removal of nitrate from drinking water has turned into a challenging duty to researchers. There are physical, chemical, and biological methods used to remove nitrate from drinking water, namely chemical denitrification process using zero capacity iron, zero capacity magnesium, ion exchange, reverse osmosis, electro dialysis, and biologic denitrification (Jae-Hee Ahn *et al.* 2008).

Nonetheless, the available technology applied to remove nitrate include shortcomings and limitations, expensiveness, low-impact, and side products can be regarded as its other deficiencies. Therefore, the direction of research has gone into the development of effective and low-cost technologies (Yunfei Xi *et al.* 2010).

Among other technologies used for water treatment, the adsorption process is in general low-cost, simply designed, as it is identified as an easy applicable technique (Sachin N. Milmile *et al.* 2011). Activated carbon has been ameliorated to remove various pollutants from aqueous solutions. At the present moment, research has grown to modify carbon level in order to increase the potentiality for its adsorption (Abbas Afkhami *et al.* 2007). Modification on carbon level may be a path to novel applications of activated carbon in order to remove specific pollutants.

2. MATERIAL AND METHODS

a) Water sample

For all experiments, the water ground of District 6 of Tehran was used, the specifications of which are given in Table-1.

Table-1. Water specifications of the water ground used.

Magnesium ($\frac{mg}{lit}$ as $CaCO_3$)	calcium ($\frac{mg}{lit}$ as $CaCO_3$)	pH	total dissolve d solids ($\frac{mg}{lit}$)	temperature (°c)	alkalinity($\frac{mg}{lit}$ as $CaCO_3$)	Total hardness ($\frac{mg}{lit}$ as $CaCO_3$)	Solphate ($\frac{mg}{lit}$)	nitrate ($\frac{mg}{lit}$)
14	310	6.8-7	399	28	324	324	116	75

Considering the fact that nitrate adsorption for different concentrations was studied in this paper, $NaNo_3$ was used to increase nitrate concentration in other experiments.

b) Absorbents and their preparation

In this paper, two different types of absorbents were used for nitrate adsorption, and their results were compared in the same condition. To prepare absorbent, rice husk and sludge of primary settling basin of sewage treatment of pulp and paper factories located in Gillan Province, Iran, were used.

The preparation of absorbents is much the same. In order to prepare activated carbon, the sludge of paper factory sewage is placed in an oven at 110 ° C for 24 hours, after partially dried by sunlight, so that it will be completely dried as it is done to avoid weight loss because of dryness. Moreover, rice husk was put into the oven after being washed in the same condition. Having been ground into powder and passed through a sieve of 600 microns, the absorbents were chemically activated in the course of Zncl2 mixture with different mass ratios for 8 hours (at ambient temperature). They were then kept in the oven at 110 ° C for 24 hours in order to be completely dry. The product was ground into powder by pounder. The powder was put in a furnace under 70 ml per minute nitrogen flow. The rate of furnace temperature increase was 10 ° C per minute, as the final temperature was 800 ° C and the duration for this temperature was 2 hours (pyrolysis operation was performed in Material and Energy Research Center in Meshkinshahr, Alborz Province). The pyrolysised powder was washed in 500 ml of molar ½ hydrochloric acid solution. Thus, it was washed several times with distilled water, so that its pH reached a constant value. It was then dried in the oven at 100 ° C for 24 hours. Finally, the activated carbon was stored in sealed glasses to be used for adsorption experiments (U.S.Orlando *et al.* 2002).

Moreover, to increase the efficiency of adsorption, all the absorbents were activated by $Zncl_2$ with various concentrations, the results of which were compared with one another.

In order to chemically activate all the absorbents, Hcl was used and kept in a mixing scenario along with the absorbents for 2 hours with respect to the level of activation.

c) Testing method

DR5000 spectrophotometer and spectroscopic method were used to read nitrate concentration in the solution. In order to investigate the effect of pH on samples, they were adjusted prior to adding adsorbents to the solution. PH adjustment in the samples is conducted using hydrochloric acid solution and normal soda. Each test was performed twice in a specific condition, and the result of adsorption would be called acceptable in case the differences between these scenarios were less than 2%.

d) Adsorption isotherm

An equilibrium ratio of the quantity of adsorbed substance to mass unit of absorbent and its equilibrium state concentration in the liquid phase at constant temperature is called adsorption isotherm. It is one of the most important parameters to realize the mechanism of adsorption. Langmuir and Freundlich isotherms are the most applicable isotherms, for which equations 1 and 2 respectively show their relationships.

Equation 1. Langmuir isotherm	$\frac{1}{q_e} = \frac{1}{Q_M} + (\frac{1}{KQ_M})(\frac{1}{C_e})$
Equation 1. Langmuir isotherm	$\frac{1}{q_e} = \frac{1}{Q_M} + (\frac{1}{KQ_M})(\frac{1}{C_e}$
Equation 2. Freundlich isotherm	$\ln(q_e) = \ln(k_f) + \frac{1}{n}.\ln(C_e)$

e) Kinetics of adsorption

It is one of the most important characteristics when dealing with the efficiency of adsorption. Several kinetic models have been proposed by researchers until now. In this paper, two models, pseudo-first-order and pseudo-second-order, were assessed for two activated carbons, one obtained from rice husk and the other from the sludge of paper industry. In order to obtain kinetic of adsorption, we need to plot adsorption graph of proposed equations and build a kinetic model based on whether or not data correspond. Pseudo-first-order and pseudo-second-order are respectively shown in equations 1 and 2.

Equation 3. Pseudo-first-order kinetic adsorption model	$\ln(q_e - q_t) = \ln(q_e) - K_f.t$
Equation 4. Pseudo-second-order kinetic adsorption model	$\frac{t}{q_t} = \frac{1}{K_s.q_e^2} + \frac{1}{q_e}.t$

3. RESULTS AND DISCUSSIONS

In this section, the results of nitrate adsorption were compared by carbon adsorbents (activated carbon obtained from rice husk and the other one from the sludge of the treatment of paper industry), and the effects of parameters such as contact time, pH, activation with $Zncl_2$, and the level of adsorbent concentration were examined.

a) The effect of pH and contact time

Figure-1 represents the ratio of nitrate adsorption level (ratio of the nitrate adsorbed in term of (mg) to the level of adsorbent in term of (gr)), to contact time (hr) for the activated carbon obtained from rice husk which was modified in a 1 to 1 ratio by $Zncl_2$.

For this figure, pH=4 is the best possible pH for this absorbent and 4 hour contact time was obtained as an equilibrium time for it. The level of nitrate adsorption in the condition equals to 80/9 (mg/gr)Experiments performed with lower pH indicated that as pH drops due to Hcl interaction added to the solution and nitrate ion with negative charge, so decreases adsorption level. The result of adsorption experiment by sugar beet pulp modified by $Zncl_2$ indicates optimal pH=4 and equilibrium time, 24 hours, and adsorption level as much as 63(mg/gr) (M.L. Hassan *et al.* 2010). Therefore, the results of the activated carbon obtained from rice husk seem very effective and appropriate with respect to a short time contact.
Moreover, Figure-2 shows the relationship between nitrate adsorption rate (mg/gr) and contact time (hr) for activated carbon by the sludge of paper industry, which was modified in 1 to 1 ratio by $Zncl_2$. This figure demonstrates that optimal pH is equal to 4 and equilibrium contact time is equal to 6 for this absorbent.

Given the fact that the nitrate ion has a negative charge, experiments on pH less than 4 revealed that adsorption level rises due to electrostatic interactions between positive surface charge and onions, as it will decline for higher pH. However, the difference of adsorption level between the pH of various acid or base solution scenarios is partially low, and given the nitrate concentration level of primary sample and the level of essential removal in order to reach a standard level, it is possible for us to reach a desired result with the same natural pH of water by consuming little energy.

The high velocity of adsorption level is due to the capacities available for adsorption for both adsorbents in early minutes. Filling these capacities, the rate of adsorption is reduced (Yuh-Shan Ho, 2005).

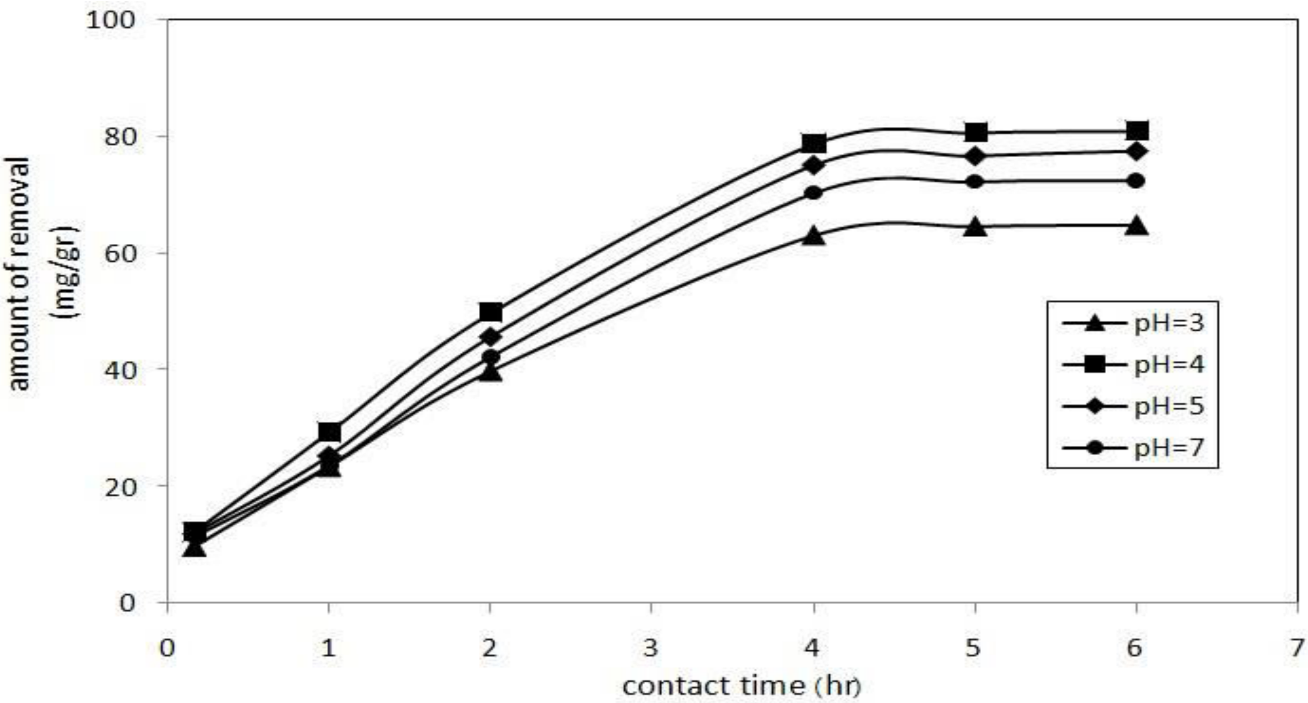

Figure-1. Nitrate adsorption versus contact time for activated carbon obtained from rice husk activated by $Zncl_2$ with 1 to 1 ratio.

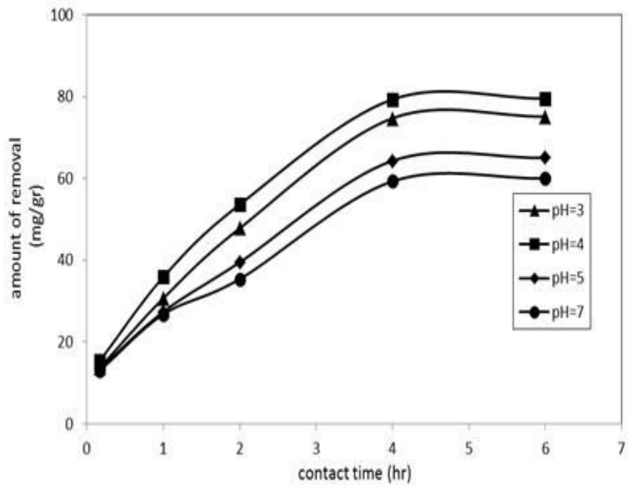

Figure-2. Nitrate adsorption versus contact time for activated carbon obtained from the sludge of paper industry activated by $Zncl_2$ in a 1 to 1 ratio.

Given the fact that the maxim quantity of adsorption occurs at pH=4 for both adsorbents, following experiments were performed at the same condition.

b) The comparison of nitrate adsorption by activated carbon obtained from rice husk and sludge of paper industry

Figure-3 shows how two absorbents work concerning nitrate adsorption at pH=4 in the same condition for activation by $Zncl_2$ in a 1 to 1 ratio. As for all carbon absorbents at 4 hour contact time, the system reached equilibrium and the level of adsorption was equal to 93.5 and 74.5(mg/gr) respectively for husk activated carbon and sludge activated carbon.

In a similar study on nitrate adsorption, conventional rice husk was used as absorbent and the level of adsorption was obtained 81.8 (mg/gr) at 48 hour contact time (U.S. Orlando *et al.* 2002). Another study on coconut shell activated by $Zncl_2$ indicated that removal of nitrate was performed as much as 10.2 (mg/gr) at a 2 hour contact time (A. Bhatnagar *et al.* 2008). Additionally, the result of a study into three absorbents, pulp of bagasse, pure cellulose, and rice husk, indicated nitrate adsorption was obtained 87.4, 83.1, and 81.8 (mg/gr) at a 48 hour contact time (U.S.Orlando *et al.*2002). In this study, the effect of pH on removal of nitrate was not examined.

Therefore, converting rice husk into activated carbon and using it as absorbent increases nitrate adsorption significantly.

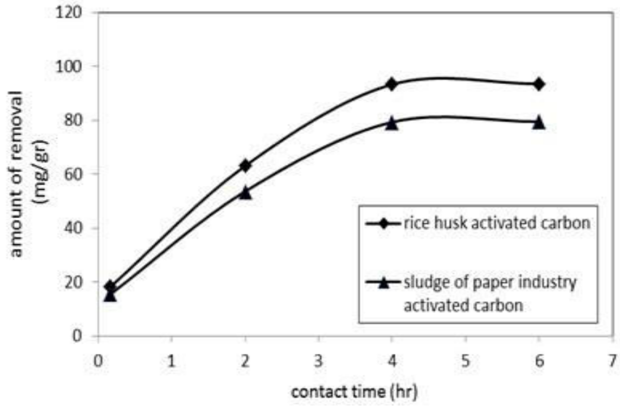

Figure-3. The comparison of carbon absorbent performance with rice husk source and sludge of paper industry with respect to removal of nitrate at the same condition, pH=4, and activation by $Zncl_2$ in a 1 to 2 ratio.

c) Effect of using $Zncl_2$

The comparison of the results of nitrate adsorption for rice husk activated carbon indicted that as for activated state by $Zncl_2$ in a 1 to 2 ratio the adsorption level is about 15% greater than the one active in a 1 to 1 ratio.

The result of the study of this sort on coconut shell concerning nitrate adsorption indicated that using $Zncl_2$ in 1 to 1 ratio would make the level of adsorption 5 times as much bigger. However, the activation was performed in two stages (before coconut shell conversion into activated carbon, and after that) at 80 °c, and the final amount of nitrate adsorption was 11.7(mg/gr) (Amit Bhatnagar *et al.* 2010). Meanwhile, concerning rice husk activated carbon absorbent, the activation by $Zncl_2$ in 1 to 1 ratio increased adsorption level by 85% in comparison to non-activated absorbent. The activation was performed just in one stage (i.e. before rice husk conversion into activated carbon) at ambient temperature. Therefore, the effect of activation by $Zncl_2$ in this case is acceptable and justifiable economically. Figure-4 shows the analogy for pH=4 and primary concentration of nitrate 100(mg/lit).

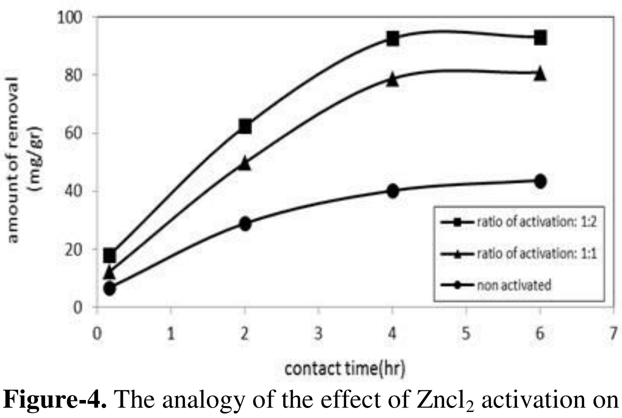

Figure-4. The analogy of the effect of $Zncl_2$ activation on the level of nitrate adsorption by activated carbon of rice husk.

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In addition, Figure-5 represents the analogy of the results of nitrate adsorption for sludge activated carbon of paper industry by $Zncl_2$ for two activated cases in 1 to 1 and 1 to 2 ratios (the ratios of absorbent mass to $Zncl_2$), and non-activated case. As for the $Zncl_2$ activated case in a 1 to 2 ratio, the adsorption level was about 18% more than the activated case in 1 to 1 ratio. However, the activation of sludge activated carbon of paper industry by $Zncl_2$ in a 1 to 1 ratio would increase adsorption level by 110% in proportion to non-activated paper industry sludge. Considering the fact that the activation for this adsorbent was conducted just in one stage at ambient temperature, it seems economical and its results can be acceptable as against the results of other researchers.

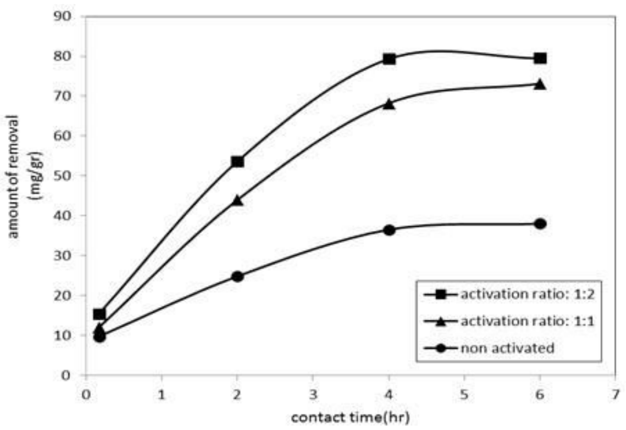

Figure-5. The analogy of the effect of Zncl2 activation on nitrate adsorption level by activated carbon obtained from sludge of paper industry.

It is worth noting that adsorption level increase in the condition for activating absorbent by $Zncl_2$ is due to an increase in micropore cavities. Moreover, in activating, $Zncl_2$ itself plays a role as an adsorbent in mesopore cavities, helping nitrate adsorption process (A. Bhatnagar *et al.* 2008).

d) The effect of adsorbent concentration level

Figure-6 and Figure-7 respectively compare the level of nitrate adsorption by rice husk activated carbon and paper industry sludge activated carbon at different adsorbent concentration. The results of the study indicated that as adsorbent concentration rises, so does adsorption level. The results of other studies also uphold the theory that as adsorbent level increases, so does the entire available surface as well as adsorption capacity (C. Namasivayam *et al.* 2005). It is evident that such adsorption increase is limited, because nitrate concentration exists in low quantity in water.

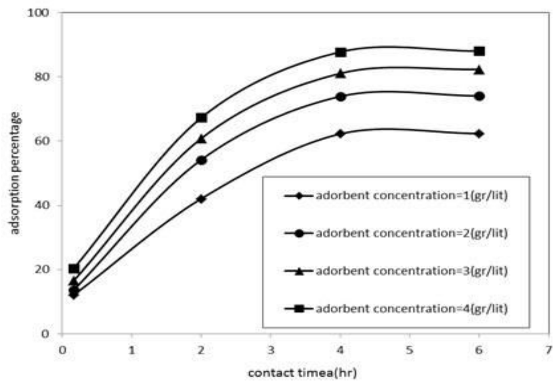

Figure-6. The analogy of nitrate adsorption by rice husk carbon activated by $Zncl_2$ in a 1 to 2 ratio in pH=4 at various adsorbent concentrations.

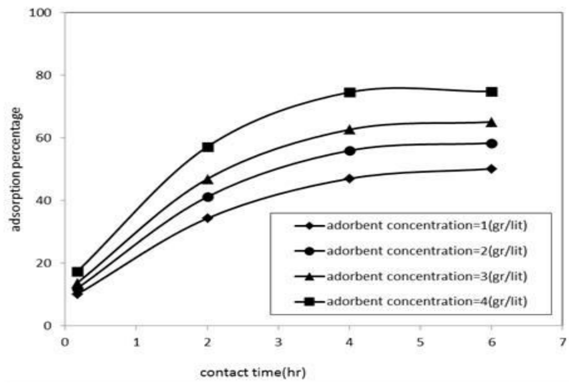

Figure-7. The analogy of nitrate adsorption by paper industry sludge carbon activated by $Zncl_2$ in a 1 to 2 ratio in pH=4 at various adsorbent concentrations.

e) Examining an isotherm for nitrate adsorption

Figures-8 and Figure-9 respectively show Langmuir isotherm and Freundlich isotherm graphs representing nitrate adsorption by carbons activated by rice husk and sludge of paper industry at $Zncl_2$ activation state.

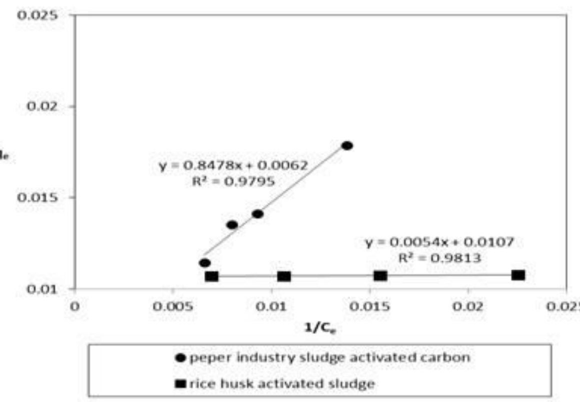

Figure-8. Langmuir isotherm for rice husk activated carbon and paper industry sludge activated carbon in pH=4.

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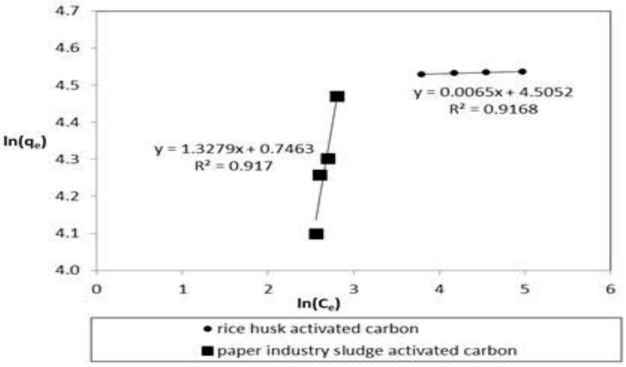

Figure-9. Freundlich isotherm for rice husk activated carbon and paper industry sludge activated carbon in pH=4.

Furthermore, Table-2 shows coefficients of the isotherms for both the adsorbents. The results indicated that the results of adsorption correspond more with Langmuir isotherm.

Table-2. Coefficients of Langmuir and Freundlich isotherms and the regression coefficient of rice husk activated carbon and paper industry sludge activated carbon at a modified state by $Zncl_2$ in a 1 to 2 ratio in pH=4.

R^2=0/9813	Q_0 =93/46 ($\frac{mg}{gr}$)	b =1/98 ($\frac{lit}{mg}$)	Rice husk activated carbon	Coefficients of Langmuir isotherm
R^2=0/9795	Q_0 =263/2($\frac{mg}{gr}$)	b =0/0032($\frac{lit}{mg}$)	Paper industry sludge activated carbon	
R^2=0/9168	n =153/85	K_f =90/49	Rice husk activated carbon	Coefficients of Freundlich isotherm
R^2=0/9170	n =1/ 343	K_f =2/085	Paper industry sludge activated carbon	

f) Examining kinetics of adsorption

Table-3 and 4 show fixed values and regression coefficients of pseudo-first and second-order kinetic models for rice husk activated carbon and paper industry sludge activated carbon respectively at three different concentrations, 100, 150, 200, (mg/lit).

Table-3. Fixed values and regression coefficients of the adsorption kinetics of pseudo- first and second- order model for nitrate adsorption by activated carbon activated by $Zncl_2$ in a 1 to 2 ratio obtained from rice husk at various nitrate concentrations.

Pseudo second order				Pseudo first order					
Difference q_e(real) and q_e(cal)	R^2	q_e(cal) (mg/gr)	K_s (×10^{-4}) (gr.mg^{-1}.min^{-1})	Difference q_e(real) and q_e(cal)	R^2	q_e(cal) (mg/gr)	K_f (×10^{-3}) (min^{-1})	q_e(real) (mg/gr)	Nitrate concentration (mg/lit)
%3/2	0/9903	96/2	1/99	%19/2	0/9903	75/3	7/6	93/2	100
%13/8	0/9652	106/4	1/73	%5/2	0/9348	88/6	12/8	93/5	150
%15/5	0/9863	107/5	2/43	%45/7	93700/	135/6	16/8	93/1	200

In order to explore the consistency of kinetic adsorption model, we need to consider regression coefficient factor (R^2) and difference in nitrate adsorption level at equilibrium state q_e(real) and concentration obtained based on q_e(real).

In a study conducted on nitrate adsorption by activated carbon obtained from coconut shell at two activated and non-activated states, the maximum difference between q_e(cal) and q_e(real) for pseudo-second-order model was 20%, while it was less than 14% in this paper, which truly confirm that the result of the experiments correspond with pseudo-second-order adsorption level.

Table-4. Fixed values and regression coefficients of the adsorption kinetics of pseudo- first and second- order model for nitrate adsorption by paper industry sludge activated carbon activated by $Zncl_2$ in a 1 to 2 ratio at various nitrate concentrations.

Pseudo second order				**Pseudo first order**					
Difference q_e(real) and q_e(cal)	**R^2**	**q_e(cal)** (mg/gr)	**K_s($\times 10^{-4}$)** (gr.mg^{-1}.min^{-1})	**Difference q_e(real) and q_e(cal)**	**R^2**	**q_e(cal)** (mg/gr)	**K_f($\times 10^{-3}$)** (min^{-1})	**q_e(real)** (mg/gr)	**Nitrate concentration** (mg/lit)
%7/1	0/9849	49/5	3/56	%3/2	0/8910	47/7	8/7	46/2	100
%8/0	0/9914	65/4	2/37	%15/3	0/9721	60/2	4/3	71/1	150
%9/6	0/9901	74/6	2/21	%20/1	0/9044	65/5	4/2	82/5	200

As can be noticed from the above table, as for the absorbent, the results of the experiments correspond more with pseudo-second-order adsorption model.

The results of the tests performed by other researchers also indicate that pseudo-second-order adsorption level can finely interpret adsorption process in the most tests (Amit Bhatnagar *et al.* 2008).

4. CONCLUSIONS

The results of the studies demonstrated that both activated carbon adsorbents, obtained from rice husk and sludge of paper industry wastewater treatment, have high efficiency in adsorbing nitrate. Given a partially low equilibrium contact time and partially high adsorption level as against other relevant studies, both adsorbents exhibited quite reasonable functionality for removal of nitrate.

The use of $Zncl_2$ has a positive effect on nitrate adsorption level. As adsorbent concentration rises, so does nitrate adsorption; however, this is limited.

The results of adsorption by both adsorbent correspond with Langmuir adsorption isotherm, and pseudo-second-order kinetic model could reasonably delineate adsorption speed run by both adsorbents. However, as for each groundwater sample which requires decreasing nitrate concentration and bringing it to the permissible level, it is imperative to choose the best adsorbent, pH, and economical contact time with respect to primary concentration, and essential adsorption level, as well as economic considerations.

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