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Amit Bhatnagar[a]; Minkyu Ji[a]; Yang-Hun Choi[a]; Woosik Jung[a]; Sang-Hun Lee[b]; Sun-Joon Kim[b]; Giehyeon Lee[c]; Heejun Suk[d]; Hyoung-Soo Kim[e]; Booki Min[f]; Seong-Heon Kim[a]; Byong-Hun Jeon[a]; Joon-Wun Kang[a]

[a] Department of Environmental Engineering, Yonsei University, South Korea [b] Department of Geo-environmental System Engineering, Hanyang University, Seoul, South Korea [c] Department of Earth System Sciences, Yonsei University, Seoul, South Korea [d] Groundwater and Geothermal Resources Division, Korea Institute of Geoscience & Mineral Resources, South Korea [e] Korea Institute of Water and Environment, Korea Water Resources Corporation, South Korea [f] Institute of Environment & Resources, Technical University of Denmark (DTU), Lyngby, Denmark

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**Amit Bhatnagar,[1] Minkyu Ji,[1] Yang-Hun Choi,[1]
Woosik Jung,[1] Sang-Hun Lee,[2] Sun-Joon Kim,[2]
Giehyeon Lee,[3] Heejun Suk,[6] Hyoung-Soo Kim,[4] Booki Min,[5]
Seong-Heon Kim,[1] Byong-Hun Jeon,[1] and Joon-Wun Kang[1]**

[1]Department of Environmental Engineering, Yonsei University,
South Korea
[2]Department of Geo-environmental System Engineering,
Hanyang University, Seoul, South Korea
[3]Department of Earth System Sciences, Yonsei University, Seoul,
South Korea
[4]Korea Institute of Water and Environment, Korea Water Resources
Corporation, South Korea
[5]Institute of Environment & Resources, Technical University of Denmark
(DTU), Lyngby, Denmark
[6]Groundwater and Geothermal Resources Division, Korea Institute of
Geoscience & Mineral Resources, South Korea

Abstract: Adsorption study with untreated and zinc chloride ($ZnCl_2$) treated coconut granular activated carbon (GAC) for nitrate removal from water has been carried out. Untreated coconut GAC was treated with $ZnCl_2$ and carbonized. The optimal conditions were selected by studying the influence of process variables such as chemical ratio and activation temperature. Experimental results reveal that chemical weight ratio of 200% and temperature of 500°C was found to be optimum for the maximum removal of nitrate from water. Both untreated and $ZnCl_2$ treated coconut GACs were characterized by scanning electron microscopy (SEM), Brunauer Emmett Teller (BET) N_2-gas adsorption, surface area and

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Address correspondence to Amit Bhatnagar or Byong-Hun Jeon, Department of Environmental Engineering, Yonsei University, 234 Maeji Heungeop, Wonju Gangwon-do, South Korea 220-710. E-mail: amit_b10@yahoo.co.in or bhjeon@yonsei.ac.kr

Energy Dispersive X-Ray (EDX) analysis. The comparison between untreated and $ZnCl_2$ treated GAC indicates that treatment with $ZnCl_2$ has significantly improved the adsorption efficacy of untreated GAC. The adsorption capacity of untreated and $ZnCl_2$ treated coconut GACs were found 1.7 and 10.2 mg/g, respectively. The adsorption of nitrate on $ZnCl_2$ treated coconut GAC was studied as a function of contact time, initial concentration of nitrate anion, temperature, and pH by batch mode adsorption experiments. The kinetic study reveals that equilibrium was achieved within one hour. The adsorption data conform best fit to the Langmuir isotherm. Kinetic study results reveal that present adsorption system followed a pseudo-second-order kinetics with pore-diffusion-controlled. Results of the present study recommend that the adsorption process using $ZnCl_2$ treated coconut GAC might be a promising innovative technology in future for nitrates removal from drinking water.

Keywords: Water treatment, nitrate removal, $ZnCl_2$ treated activated carbon, adsorption isotherms, kinetic modeling

INTRODUCTION

Nitrate pollution in groundwater and drinking water is of increasing environmental concern on a global scale (1). Nitrate concentrations in surface water and especially in groundwater have increased rapidly in all parts of the world since last few decades (2). The primary cause of nitrate pollution is excessive use of nitrogenous fertilizers in agricultural sector. Additional sources of nitrate pollution include wastewaters and agricultural and urban runoff, disposal of untreated sanitary and industrial wastes in unsafe manner, leakage in septic systems, landfill leachate, animal manure, airborne nitrogen compounds given off by industry and automobiles, which are deposited on the land in precipitation and dry particles (3, 4). Nitrate, due to its high water solubility (2), is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and promoting eutrophication (1, 2).

Increasing nitrate concentrations in drinking water causes two adverse health effects: induction of "blue-baby syndrome" (methemoglobinemia), especially in infants, and the potential formation of carcinogenic nitrosamines (5, 6). Recent studies (7 and references therein) have shown that excess amounts of nitrates in drinking water may also be responsible to causing diverse kinds of cancers in humans. Ward et al. (8) nicely discussed the epidemiologic evidence for drinking water nitrate and risk of specific cancers, adverse reproductive outcomes, and other health outcomes in the context of the current regulatory limit for nitrate in drinking water.

Keeping the view of serious health problems associated with excess nitrate concentrations in drinking water, US Environmental Protection Agency (US EPA) has set the maximum safe concentration of 10 mg/L of nitrate-N in drinking water (9). However, the effectiveness of this regulatory limit for preventing other health risks such as cancer has not been adequately addressed (10). In order to provide safe drinking water, it is necessary to treat water to reduce the nitrate concentrations below the permissible limits.

Nitrate removal from water is a challenging task for researchers because of its high stability and solubility (2). There are some biological and physiochemical methods for the removal of nitrates from water such as chemical denitrification using zero-valent iron (Fe^0) (11–13), zero-valent magnesium (Mg^0) (14), ionic exchange (15), reverse osmosis (16), electrodialysis (17), catalytic denitrification (18), and biological denitrification (19). However, current available technologies for nitrate removal have their own shortcomings and limitations and are found to be expensive, less effective, and they also generate additional by-products. Therefore, research is going on to develop low cost and efficient technologies for nitrate removal from water.

The adsorption process in general, is considered better among other wastewater treatment technologies because of the low cost, simple design and easy operation. Activated carbon has been proven to be the best adsorbent for the removal of various types of pollutants from aqueous solutions. Research is now being directed towards the modification of carbon surfaces to enhance their adsorption potential. Modification of the surface of activated carbons (ACs) might be a viable attractive route toward novel applications of activated carbons for the removal of specific types of contaminants.

In the present work, commercial activated carbon (produced from coconut shells by steam activation) was chemically activated with $ZnCl_2$. Chemical activation with $ZnCl_2$ produces activated carbons which are essentially microporous (20). A comparative study with untreated and $ZnCl_2$ treated coconut GAC has been performed to evaluate the adsorption potential of these two activated carbons for nitrate removal from aqueous solutions. Equilibrium and kinetic studies were performed to describe the adsorption process. The influence of several operating parameters on the adsorption of nitrate on GAC was investigated as a function of contact time, initial nitrate concentration, temperature and pH. Different kinetic models were tested to identify the adsorption mechanism and the results are presented in this communication.

EXPERIMENTAL

Materials and Methods

Standard solution of nitrate (1000 mg/L) was prepared by dissolving $NaNO_3$ (Oriental Chemical Industries, South Korea) in deionized water. A range of dilutions, 5–200 mg/L was prepared from the stock solution. The coconut activated carbon was obtained from Jacarbon. All reagents used were of analytical reagent grade.

Preparation of $ZnCl_2$ Treated Activated Carbon

Coconut granular activated carbon was used as starting material. Chemical activation of this GAC was done with $ZnCl_2$ solution. 10 g of dried GAC was well mixed, by stirring, with 100 mL of an aqueous solution that contained 10 g of $ZnCl_2$. The chemical ratio was 100% (100 mL of 10 g $ZnCl_2$/10 g GAC) in this case. The chemical ratio is defined as the weight ratio of activating agent ($ZnCl_2$) to the precursor (GAC). The mixing was performed at 80°C for 1 h. After mixing, the slurry was kept in an oven at 110°C for 24 h. The resulting $ZnCl_2$ treated sample was then heated at different temperatures in a furnace in air atmosphere for 1 h. After activation, sample was allowed to cool and subsequently washed with 0.5 M HCl and then several times with deionized water. The resulting product was kept in a desiccator for further use. The experiments were carried out for different chemical ratio (100–300%) and carbonization temperature (400–600°C).

Adsorption Studies

The adsorption of nitrate on untreated and $ZnCl_2$ treated coconut GACs was studied at room temperature ($25 \pm 2°C$) by batch experiments. 10 mL of nitrate solution of varying initial concentrations (5–200 mg/L) in 50 mL capped glass tubes was shaken with 0.1 g of adsorbent for a specified period of contact time in a temperature controlled shaking assembly (Jeio Tech Co., SWB-20 shaking water bath). After equilibrium, samples were filtered using 0.2 μm filters (Versapor, Pall Co., USA) and the concentration of the nitrate was determined by ion chromatography (Dionex, DX-120). Reproducibility of the measurements was determined in triplicates and the average values are reported. Relative standard deviations were found to be within ±3.0%. The pH of the solutions was measured before and after the equilibration and a slight change in pH was observed. The pH of blank nitrate solutions (5–200 mg/L) was observed 6.0–6.4, and after adding the $ZnCl_2$ treated coconut GAC, it was 5.4–5.6. The amount of nitrate adsorbed (q_e in mg/g) was determined as follows:

$$q_e = (C_o - C_f)V/m \qquad (1)$$

where C_o and C_f are the initial and final concentrations of the nitrate in solution (mg/L), V is the volume of solution (L) and m is the mass of the adsorbent (g). The adsorption was studied as a function of contact time, initial nitrate concentration, temperature, and pH.

RESULTS AND DISCUSSION

Effects of Chemical Ratio and Carbonization Temperature

Experiments were performed at different chemical weight ratios (activating agent/precursor) viz., 100%, 200%, and 300% in order to see the influence of chemical ratio on the adsorption of nitrate by GAC and results are shown in Fig. 1. It is seen from the figure that the highest amount adsorbed (10.2 mg/g) of nitrate was found at a chemical ratio of 200% (Fig. 1) while a lower adsorption of nitrate was found at impregnation ratio of 100% and 300%. As the chemical weight ratio of 200% showed maximum adsorption of nitrate, therefore, this weight ratio (200%) was selected for all further studies. Other researchers (21) also selected chemical ratio of 200% in their study while preparing the activated carbons from bituminous coals with $ZnCl_2$ activation.

In order to see the influence of carbonization temperature on the adsorption capacity of GAC for nitrate removal, experiments were conducted at three carbonization temperatures viz., 400, 500, and 600°C and results are shown in Fig. 2. It is seen from the figure that lower adsorption of nitrate was found at 400 and 600°C (carbonization temperatures) while adsorption was maximum at 500°C (Fig. 2). The lower adsorption of nitrate with GAC prepared at 400°C carbonization temperature can be attributed to the inadequacy of heat energy generated at low carbonization temperature for any substantial evolution of volatile matters essential for pore development. At 500°C, more volatile matters were released progressively during carbonization, thereby resulting in the development of some new pores (22, 23), and hence the adsorption of

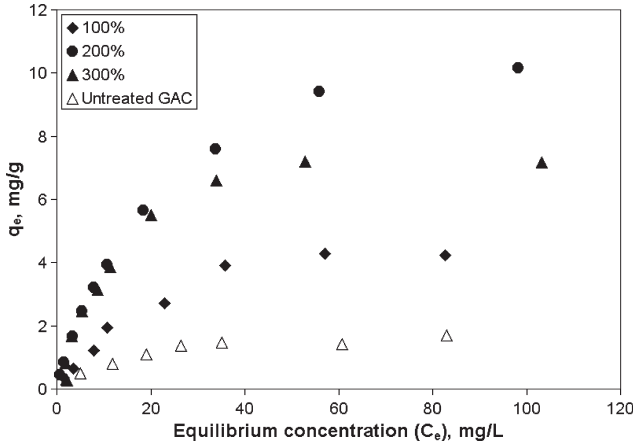

Figure 1. Effect of chemical ratio on adsorption of nitrate on coconut activated carbon (temperature = 25°C, contact time = 2 h, GAC dosage = 0.1 g/10 mL, pH = 5.5, carbonization temperature = 500°C).

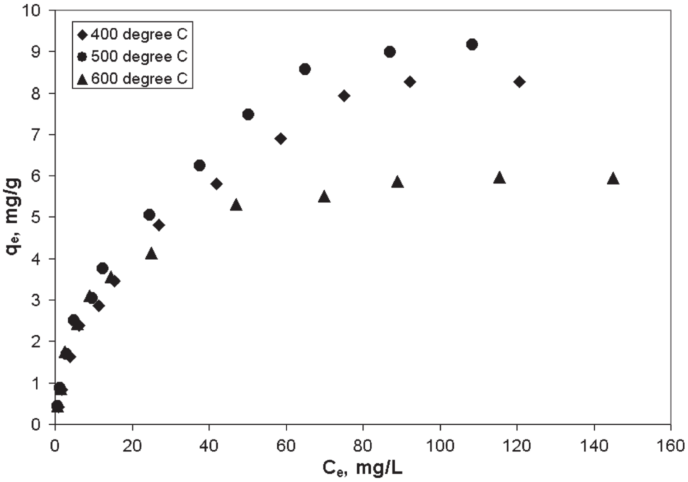

Figure 2. Effect of carbonization temperature on adsorption of nitrate on coconut activated carbon (chemical weight ratio = 200%, temperature = 25°C, contact time = 2 h, GAC dosage = 0.1 g/10 mL, pH = 5.5).

nitrates increased progressively. The decrease in the adsorption of nitrates with further increase in carbonization temperature to 600°C might be due to a sintering effect at high temperature, followed by shrinkage of the char, and realignment of the carbon structure, which resulted in reduced pore areas as well as volume (23, 24). As carbonization temperature of 500°C showed maximum adsorption of nitrate among our experimental results, therefore the carbonization temperature of 500°C was selected for all further studies. A temperature of 500°C for $ZnCl_2$ activation has also been recommended by other researchers (25).

Characterization of Untreated and $ZnCl_2$ Treated Activated Carbon

The untreated and $ZnCl_2$ treated coconut GACs were characterized and the characteristics of both activated carbons were compared. The BET surface area of untreated and $ZnCl_2$ treated coconut GACs were found 1144 and 893 m^2/g, respectively. The decrease in surface area in $ZnCl_2$ treated GAC can be explained due to the formation of zinc oxide which significantly covered the pore openings of activated carbon resulting in lower surface area for $ZnCl_2$ treated GAC. Untreated and $ZnCl_2$ treated GACs were analyzed by X-ray diffraction (XRD) in order to identify the mineral phases formed onto the GAC after $ZnCl_2$ treatment but no difference was observed between untreated and $ZnCl_2$ treated GAC. The morphology of untreated

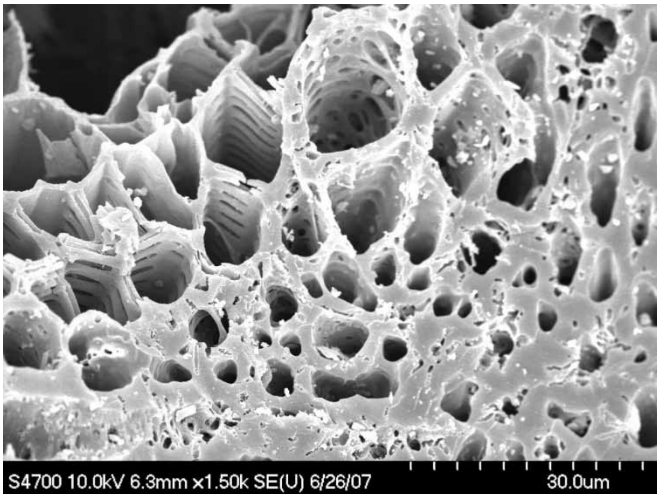

Figure 3. Scanning electron micrograph (SEM) of untreated coconut GAC.

and $ZnCl_2$ treated coconut GACs was analyzed by scanning electron micrographs (SEM) and images are shown in Figs. 3 and 4. It is clear from SEM image of untreated GAC (Fig. 3) that it has porous structure containing macro-, meso-, and micropores in it. After treating with $ZnCl_2$, macro- and mesopores were occupied by some of the zinc oxide (needle like structure visible in Fig. 4) by giving higher microporosity in $ZnCl_2$ treated GAC. It is also evident by micropore volume data that the micropore volume increased

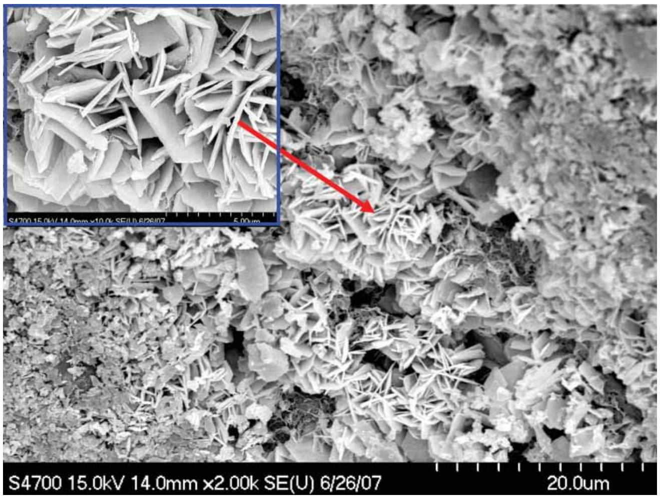

Figure 4. Scanning electron micrograph (SEM) of $ZnCl_2$ treated coconut GAC.

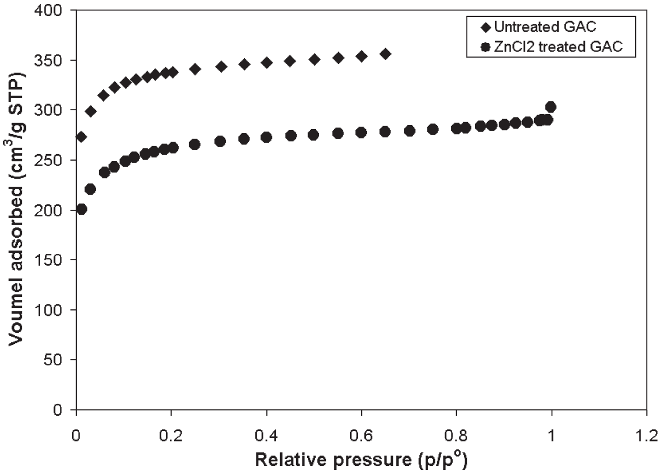

Figure 5. N_2 adsorption isotherm of untreated and $ZnCl_2$ treated GAC.

from 0.4159 (in untreated GAC) to 0.4468 cm^3/g (in $ZnCl_2$ treated GAC). EDX analysis data showed 89.65% C, 5.64% O, 0.69% Cl, and 4.02% Zn (all values in wt%) in untreated GAC. However, the carbon content was decreased from 89.65% to 66.39% in $ZnCl_2$ treated GAC sample, while oxygen, chloride, and the zinc contents were increased from 5.64% to 14.26%, 0.69% to 7.26%, and 4.02% to 12.09% respectively in $ZnCl_2$ treated GAC sample. A typical N_2 adsorption isotherm of untreated and $ZnCl_2$ treated coconut GACs is shown in Fig. 5. It is clear from the figure that nitrogen adsorption decreases in $ZnCl_2$ treated GAC sample. This may be attributed to the fact that some zinc oxide was trapped into the pores of GAC, which could possibly block the entrance of pores to some extent, thereby reducing the number of available pores for nitrogen adsorption and inhibiting the adsorption of N_2 molecules into GAC. These results are consistent with BET surface area where lower surface area was observed for $ZnCl_2$ treated GAC (894 m^2/g) compared with untreated GAC (1144 m^2/g).

Effect of Contact Time and Concentration

In order to establish the equilibration time for maximum adsorption of nitrate and to know the kinetics of the adsorption process, the adsorption of nitrate on $ZnCl_2$ treated coconut GAC was studied as a function of contact time and the results are shown in Fig. 6. The experimental conditions for this experiment were as follows: initial concentration of nitrate solution = 50 mg/L; adsorbent does = 0.1 g; room temperature = 25 ± 2°C; pH = 5.5–6.5. It is seen from Fig. 6 that rate of uptake of nitrate was rapid in the beginning and 50% adsorption was completed within 10 min. It is also seen from

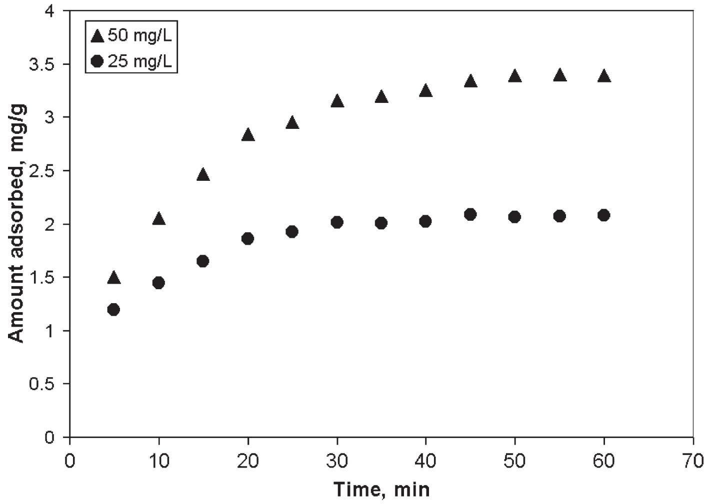

Figure 6. Effect of contact time and concentration on adsorption of nitrate on $ZnCl_2$ treated coconut GAC (temperature = 25°C, GAC dosage = 0.1 g/10 mL, pH = 5.5).

Fig. 6 that the time required for equilibrium adsorption is ~60 min, and the equilibration period of 2 h was selected for further experiments.

The effect of concentration on equilibrium time was also investigated at two different concentrations (25 mg/L and 50 mg/L) and results are also shown in Fig. 6.

Kinetic Modeling

Kinetics of adsorption is one of the important characteristics in defining the efficiency of adsorption. Various kinetic models have been proposed by different researchers. In the present study, we applied four simplified kinetic models viz pseudo-first-order, pseudo-second-order, Weber and Morris, and Bangham's models in order to investigate the mechanism of adsorption of nitrate on $ZnCl_2$ treated GAC.

Pseudo-First-Order Model

Various reports (26, 27) exist where adsorption has been considered as pseudo-first-order. The Lagergren's rate equation (28) is the one most widely used (29–31) for the sorption of a solute from a liquid solution. Thus this first order equation:

$$\log(q_e - q) = \log q_e - \frac{k_f}{2.303} t \tag{2}$$

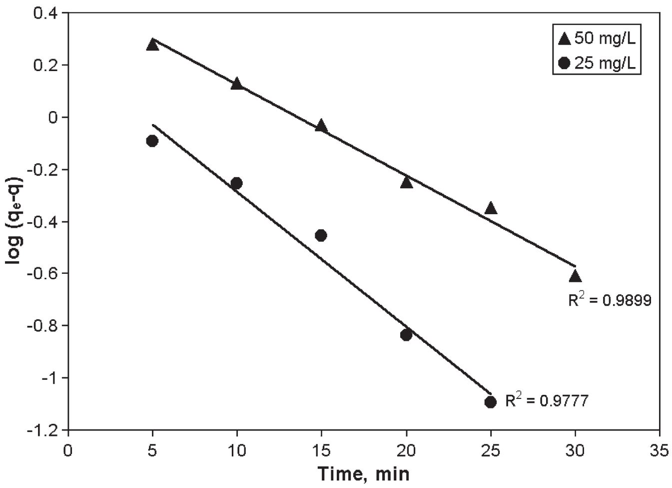

Figure 7. Pseudo-first-order kinetic plots of adsorption of nitrate on $ZnCl_2$ treated coconut GAC.

where "q_e" and "q" are the amount of nitrate adsorbed (mg/g) at equilibrium and at time t, respectively, and k_f the pseudo-first-order rate constant, was applied to the present study of nitrate adsorption. Figure 7 shows a plot of linearized form of pseudo-first-order model at two concentrations studied. The slope and intercept of plot of log ($q_e - q$) versus t were used to determine the pseudo-first-order rate constants (k_f) and $q_{e(cal)}$ and are compiled in Table 1 along with correlation coefficients (R^2) values. It was observed that the correlation coefficients (R^2) for the pseudo-first-order kinetic model were less than 0.99 at two concentrations studied and the calculated q_e values $q_{e(cal)}$ for the pseudo-first-order model did not give reasonable values with regard to the experimental uptake values $q_{e(exp)}$. This suggests that present adsorption system did not follow pseudo-first-order kinetics. Similar results were also reported by other workers (32, 33) while investigating the adsorption of nitrate on various materials viz. activated carbon, sepiolite, sepiolite activated by HCl and slag (32) and $ZnCl_2$ activated carbon prepared from coconut coir pith (33).

Pseudo-Second-Order Model

The adsorption kinetics was also described as pseudo-second-order process (34–36).

$$\frac{t}{q_t} = \frac{1}{k_s q_2^e} + \frac{1}{q_e} t \tag{3}$$

Table 1. Comparison of pseudo-first-order, pseudo-second-order, Weber and Morris and Bangham's models parameters, and calculated ($q_{e(cal)}$) and experimental ($q_{e(exp)}$) values for different initial nitrate concentrations

		Pseudo-first-order model			Pseudo-second-order model			Weber and Morris model		Bangham's model		
C_i (mg/L)	$q_{e(exp)}$ (mg/g)	$K_f \times 10^{-1}$ (1/min)	$q_{e(cal)}$ (mg/g)	R^2	$K_s \times 10^{-2}$ (g/mg min)	$q_{e(cal)}$ (mg/g)	R^2	k_{ip} (mg/g $\cdot$ min$^{1/2}$)	R^2	k_o	α	R^2
25	2.07	1.19	1.69	0.9777	7.91	2.32	0.9938	0.27	0.9864	14.05	0.52	0.9989
50	3.40	0.80	2.95	0.9899	2.60	4.10	0.9962	0.51	0.9846	28.10	0.58	0.9960

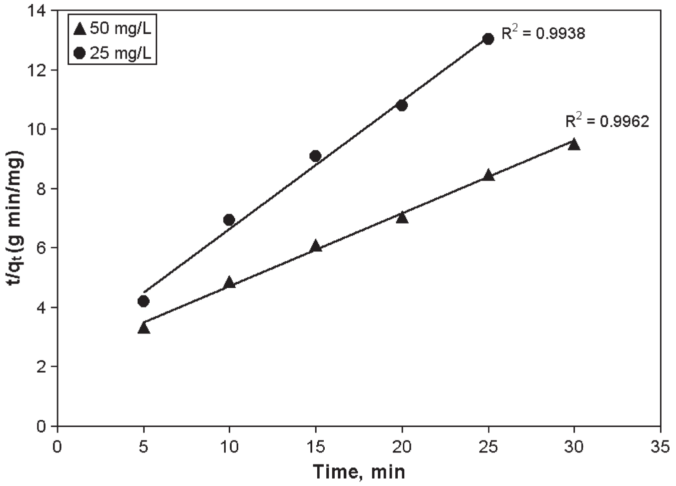

Figure 8. Pseudo-second-order kinetic plots of adsorption of nitrate on $ZnCl_2$ treated coconut GAC.

where "q_e" and "q_t" are the amount of nitrate adsorbed (mg/g) at equilibrium and at time t and k_s is the rate constant of pseudo-second-order adsorption. The plots between t/q_t versus t were drawn and are shown in Fig. 8. The slope and intercept of plot of t/q_t versus t were used to determine the pseudo-second-order rate constants (k_s) and $q_{e(cal)}$ and are compiled in Table 1 along with correlation coefficients (R^2) values. As can be seen from Table 1, the theoretical $q_{e(cal)}$ values agree well with the experimental $q_{e(exp)}$ ones in the case of pseudo-second-order kinetic model with good correlation coefficients (higher than 0.99) at two concentrations studied. This suggests that the present adsorption system can be defined more favorably by the pseudo-second-order kinetic model. Similar results were also reported by other workers (32, 33) where adsorption of nitrate followed pseudo-second order kinetics on various materials (32) and $ZnCl_2$-activated carbon prepared from coconut coir pith (33).

There are essentially three consecutive mass transport steps associated with the adsorption of solute from the solution by an adsorbent. These are

i. film diffusion
ii. intraparticle or pore diffusion, and
iii. sorption into interior sites.

The third step is very rapid and hence film and pore transports are the major steps controlling the rate of adsorption. In order to understand the diffusion mechanism, different diffusion models were tested to the present nitrate adsorption study.

Weber and Morris Model

Kinetic data (Fig. 6) was analyzed in the light of intraparticle diffusion model proposed by Weber and Morris (37):

$$q_t = k_{ip} t^{1/2} + C \tag{4}$$

where, C is the intercept and k_{ip} is the intraparticle diffusion rate constant. According to Eq. 4, a plot of uptake (q_t) versus the square root of t, $(t^{1/2})$ should be linear when adsorption mechanism follows the intraparticle diffusion process. Figure 9 shows a plot of linearized form of intraparticle diffusion model. As can be seen from Fig. 9, the intercept of the line (Fig. 9), do not pass through the origin and the correlation coefficients (R^2) are less than 0.99 at two concentrations studied indicating that the mechanism of nitrate adsorption onto adsorbent does not follow Weber and Morris model. The rate parameters, $k_{ip,}$ together with correlation coefficients were calculated and are listed in Table 1.

Bangham's Model

Kinetic data were further analyzed in the light of following Bangham's equation (38)

$$\log\log\left(\frac{C'_o}{C'_o - q'm'}\right) = \log\left(\frac{k_o m'}{2.303\ V}\right) + \alpha \log \mathrm{t} \tag{5}$$

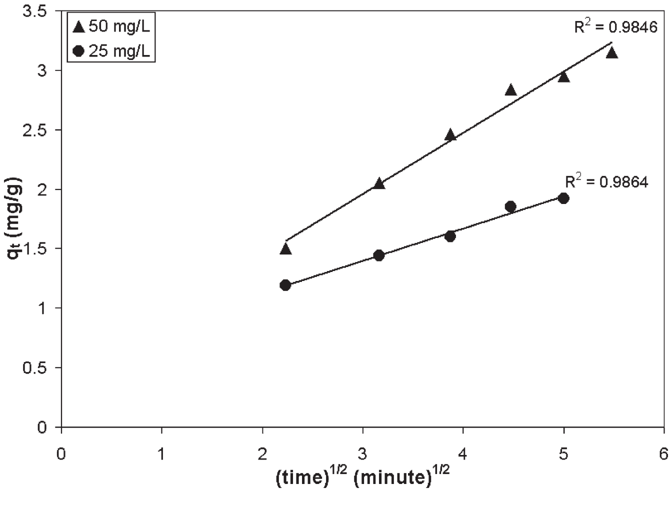

Figure 9. Weber and Morris intraparticle diffusion plots of adsorption of nitrate on $ZnCl_2$ treated coconut GAC.

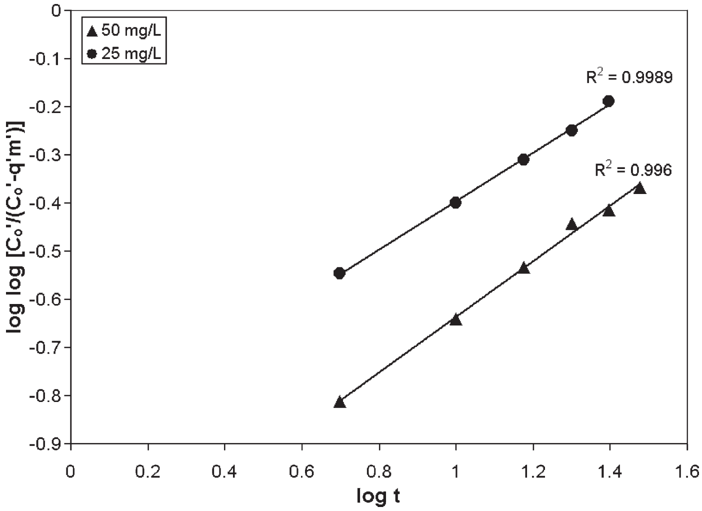

Figure 10. Bangham's pore diffusion plots of adsorption of nitrate on $ZnCl_2$ treated coconut GAC.

where C_o' is the initial concentration of the adsorbate in solution (mmol/L), V the volume of the solution (mL), m' the weight of adsorbent used per liter of solution (g/L), q' (mmol/g) the amount of adsorbate retained at time t, and α (<1) and k_o constants, to present nitrate adsorption studies were used. As such log log $[C_o'/(C_o' - q'\ m')]$ was plotted against log t in Fig. 10. The linearity of these plots with good correlation coefficients (higher than 0.99) at two concentrations studied confirms the applicability of Bangham's model in the present adsorption study and indicates that the diffusion into pores of the adsorbent controls the adsorption process.

Adsorption Isotherms

In order to evaluate the efficacy of the untreated and $ZnCl_2$ treated coconut GAC for nitrate removal, the equilibrium adsorption of nitrate was studied as a function of nitrate concentration ($C_i = 5-200$ mg/L) and the adsorption isotherms of nitrate are shown in Fig. 11. The comparison between untreated and $ZnCl_2$ treated activated carbons clearly reveals that treatment with $ZnCl_2$ has significantly improved the adsorption efficacy of activated carbon. Efficiency of $ZnCl_2$ treated coconut GAC was increased up to 6 fold compared to untreated GAC. The adsorption capacities were found 1.7 mg/g for untreated GAC and 10.2 mg/g for $ZnCl_2$ treated GAC.

It is interesting to note here that the surface area is not an important factor for the adsorption of nitrate by GAC. Carbon surface alone does not favor higher adsorption of nitrate and lower adsorption (1.7 mg/g) of nitrate was

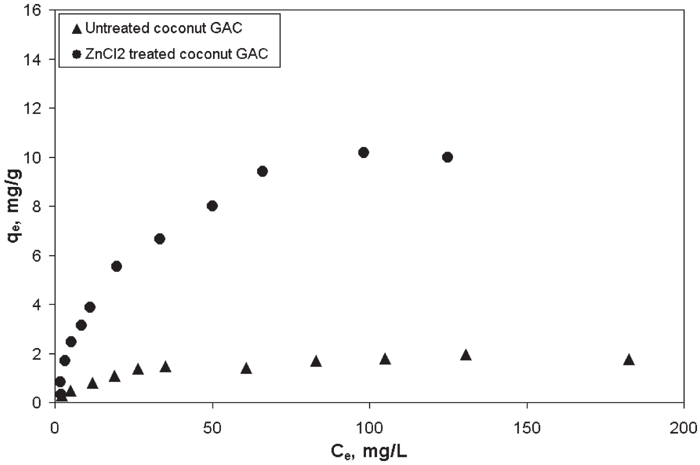

Figure 11. Adsorption isotherms of nitrate adsorption on untreated and $ZnCl_2$ treated coconut GAC (temperature = 25°C, contact time = 2 h, GAC dosage = 0.1 g/10 mL, pH = 5.5).

found on untreated GAC in spite of its higher surface area (1144 m^2/g). On the other hand, $ZnCl_2$ treated GAC which has lower surface area (893 m^2/g) showed higher adsorption of nitrate (10.2 mg/g). This behavior can be explained by two facts. First, more micropores were formed after treatment with $ZnCl_2$ as it is well known that $ZnCl_2$ promotes the microporosity in GAC (20). Second, the presence of zinc oxide (formed in macro- and mesopores) also acted as adsorbent for the sorption of nitrate anions. Therefore, both these factors

i. increased microporosity and
ii. formation of zinc oxide in macro- and mesopores enhanced the nitrate adsorption in $ZnCl_2$ treated GAC. Sorption site density of nitrate per nm^2 was also calculated and it was found 1.42×10^{-2} NO_3^-/nm^2 for untreated GAC and 11.1×10^{-2} NO_3^-/nm^2 for $ZnCl_2$ treated GAC.

The sorption site density of nitrate in $ZnCl_2$ treated GAC was found ca. 8 fold greater compared to the untreated GAC. These results support our experimental data where higher nitrate adsorption was observed on $ZnCl_2$ treated GAC in spite of having lower surface area (893 m^2/g).

Effect of Temperature

In order to understand the effect of temperature on the adsorption of nitrate, experiments were also conducted at 10 and 45°C and results are shown in

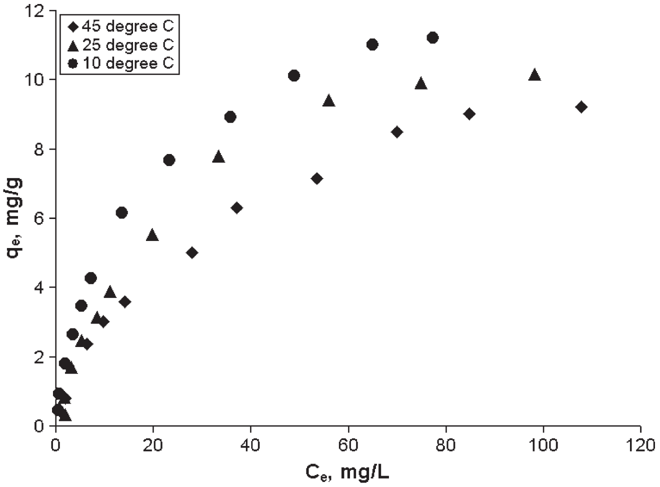

Figure 12. Effect of temperature on nitrate adsorption on $ZnCl_2$ treated coconut GAC (contact time = 2 h, GAC dosage = 0.1 g/10 mL, pH = 5.5).

Fig. 12. A comparison of adsorption isotherms at 10°, 25°, and 45°C shows that adsorption slightly decreases by increasing the temperature.

The most widely used isotherm equation, the Langmuir model, was used to describe the experimental data of adsorption isotherms and for the equilibrium modeling. The linearized Langmuir equation has the following form (39)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \qquad (6)$$

where "q_e" is amount adsorbed at equilibrium concentration "C_e", "q_m" the Langmuir constant representing maximum monolayer adsorption capacity and "b" is the Langmuir constant related to energy of adsorption. The plots of $1/q_e$ as a function of $1/C_e$ for the adsorption of nitrate were drawn and are shown in Fig. 13. The linearity of these plots with good correlation coefficients (R^2) varying from 0.9872 to 0.9985 confirm the applicability of Langmuir model in the present adsorption system.

The values of monolayer capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 2. It is seen from Table 2 that the monolayer capacity (q_m) of the adsorbent for the nitrate is comparable to the maximum adsorption obtained from adsorption isotherms.

The influence of adsorption isotherm shape has been discussed (40) to know whether adsorption is favorable or not in terms of "R_L", a dimensionless

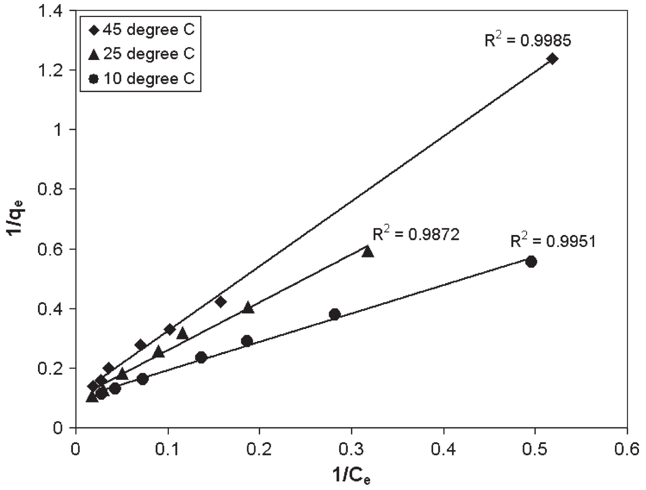

Figure 13. Langmuir plots of nitrate adsorption on $ZnCl_2$ treated coconut GAC.

constant referred to as separation factor or equilibrium parameter. "R_L" is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

The values of "R_L" calculated as per above equation are incorporated in Table 2. All the "R_L" values lie between 0 and 1 confirming that the adsorption isotherm is favorable.

Thermodynamic parameters were calculated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The thermodynamic parameters were

Table 2. Langmuir constants and separation factor for the adsorption of nitrate on $ZnCl_2$ treated coconut GAC at different temperatures

Temperature (°C)	q_m (mg/g)	b (L/mol)	R_L
10	10.37	5.49	0.71×10^{-2}
25	10.26	3.41	1.21×10^{-2}
45	9.35	2.83	1.35×10^{-2}

Table 3. Thermodynamic parameters for the adsorption of nitrate on $ZnCl_2$ treated coconut GAC at different temperatures

Temperature (°C)	ΔG^0 (kJ/mol)	ΔS^0 (J/mol · K)	ΔH^0 (kJ/mol)
10	−4.01	−32.33	
25	−3.05	−33.93	− 13.16
45	−2.75	−32.74	

calculated using the following equations (41):

$$\Delta G^0 = -RT \ln (b) \tag{8}$$

$$\ln(b_2/b_1) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{9}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

where, "b" is a Langmuir constant (L/mol) at temperature T (K); R is an ideal gas constant (8.314 J/mol. K); ΔG^0 and ΔH^0 are in J/mol; ΔS^0 in J/mol. K. The parameters calculated are summarized in Table 3. It is known that the absolute magnitude of the change in free energy (ΔG^0) for physisorption is between −20 and 0 kJ/mol; chemisorption has a range of −80 to −400 kJ/mol (42, 43). ΔG^0 values were calculated to be −4.01, −3.05 and −2.75 kJ/mol for 10, 25 and 45 °C, respectively (Table 3). This implies that the adsorption of nitrate onto $ZnCl_2$ treated GAC may occur as physically. The negative values of ΔG^0 at various temperatures show the spontaneous nature of the adsorption process.

The value of standard enthalpy change (ΔH^0) for nitrate adsorption is −13.16 kJ/mol that is, interactions between nitrate and $ZnCl_2$ treated GAC is exothermic in nature. In literature (37), when the value of ΔH^0 is lower than 40 kJ/mol the type of adsorption can be accepted as a physical process. Since ΔH^0 value obtained in this study is lower than 40 kJ/mol, it would be claimed that the physical adsorption occurs during adsorption. Since nitrate anions are not arranged in an ordered manner in solution phase, the standard entropy change (ΔS^0) for adsorption process is negative. In other words, degrees of freedom of the adsorbed species are decreasing.

Effect of pH

The initial concentration of 50 mg/L of nitrate was used to examine the effect of pH on nitrate removal and the results are shown in Fig. 14. Maximum

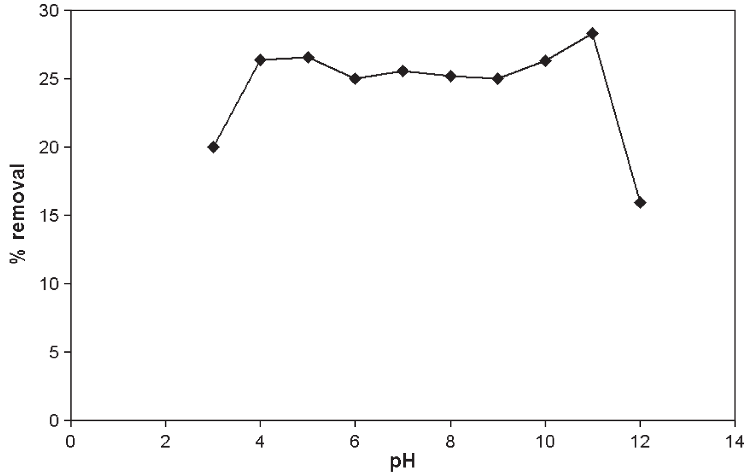

Figure 14. Effect of pH on nitrate adsorption on $ZnCl_2$ treated coconut GAC ($C_i = 50$ mg/L, temperature = 25°C, contact time = 2 h, GAC dosage = 0.1 g/10 mL).

percent removal of nitrate occurred between pH 4–11. Lower pH (pH 3.0) did not favor the higher adsorption of nitrate which might be due to the competition of Cl^- ions (from HCl added externally to adjust the pH) with nitrate anions for the adsorbent sites (33). Further, at highly basic pH, when the adsorbent is highly negatively charged, adsorption of nitrate was decreased due to electrostatic repulsion between the negatively charged adsorbent surface and the nitrate anion (33).

CONCLUSIONS

The results of the present study carried out on the adsorption of nitrate on untreated and $ZnCl_2$ treated coconut GAC lead to the following conclusions:

- $ZnCl_2$ treatment significantly improved the adsorption potential of untreated GAC.
- Chemical ratio (activating agent/precursor) of 200% and temperature of 500°C was found to be optimum for the maximum removal of nitrate from water.
- The adsorption capacities of untreated and $ZnCl_2$ treated coconut GACs were 1.7 and 10.2 mg/g, respectively.
- The adsorption data conform best to the Langmuir isotherm.
- Kinetic study results indicate that the present adsorption system followed a pseudo-second-order kinetics with pore-diffusion-controlled.

- $ZnCl_2$ treated coconut GAC can be fruitfully used for nitrates removal from drinking water.

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