

Application of sugarcane straw anion exchanger for nitrate removal

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Abstract: The effect of sugarcane straw-AE of micrometer and nanometer particle sizes on nitrate removal by batch and column experiments has been investigated. The effects of operating conditions such as pH, adsorbent dosage, initial anion concentration, the coexisting ions and desorption experiments were examined. The results showed that the optimum pH=6 and the equilibrium time was 3h and 2h for micrometer-(μm) and nanometer-(nm) sized sugarcane straw-AE, respectively. The effect of initial concentration of NO_3^- ions with varying solution NO_3^- concentrations 5, 15, 50, 80, and 120 mg/L at optimum pH and time was investigated. With increasing initial NO_3^- concentration, R% from 78% to 60% and 87% to 80% decreased for micrometer and nanometer sized sugarcane straw-AE, respectively. With the increase of adsorbent dose from 0.1 to 0.5 g, for micrometer and nanometer sized sugarcane straw-AE, the R% increased from 43% to 69% and 52% to 71% respectively, but remained almost unchanged when adsorbent dosage ranged from 0.5 to 1g. Adsorption isotherm of nitrate ions onto sugarcane straw-AE fitted Langmuir isotherm model well. Adsorption kinetics of nitrate ions could be most successfully described by the pseudo-second order model. In column experiment, q_e for micrometer and nanometer sized sugarcane straw-AE obtained 3.84, 11.57, 24.54 mg/g and 6.99, 12.7, 17.28 mg/g, respectively. This study indicated that sugarcane straw-AE could be used for the removal of nitrate ions in water treatment.

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1. Introduction

Nitrate pollution in surface and ground water has become a gradually more important problem for all over the world. An increased nitrate concentration supplies presents a potential health hazard such as blue baby. Several methods for nitrate removal from wastewater are denitrification, selective ion exchange and ammonia stripping (Fernandez-Olmo et al., 2007; Uygur and Karg, 2004). Ion exchange is a very feasible process for treatment of underground and surface water, primarily due to its ease of application (Malekian, 2011). Recently, numerous attempts have been made in finding economical and effective ion exchangers produced from agricultural by-products. So, several materials such as sugarcane bagasse (Orlando et al., 2003) and peanut hull (Gong et al., 2005) could be modified into anion exchangers and utilized for this purpose. Cross linking agricultural by-products with epichlorohydrin is the most common method used in the preparation of agricultural by-products based anion exchangers (Ozturk and EnnilKose, 2008). In this work, anion exchangers based on aminated intermediate (epoxypropyl triethylammonium chloride, ETC) is prepared (Xing et al., 2010), then micrometer and nanometer sized sugarcane straw-AE on nitrate removal investigated.

The objectives were in this study (1) determination of optimum condition nitrate removal (2) determination of the effect of particle size on NO_3^- removal and (3) determination of NO_3^- removal by sugarcane straw-AE and identification of an empirical model that best describes this ion-exchange process.

2. Experimental

2.1. Sugarcane straw sample

The Sugarcane straw used in this study originated from Khuzestan province, Iran. Total elemental analysis was performed by edax analysis showed that the Sugarcane straw had the following chemical composition (in %): Mg=3.64, Na=0.9, Si=11.74, S=8.72, Cl=7.06, Ca=2.33, Zn=71.6 and K=2.65 (Figure 1). The particle size of Sugarcane straw was between 120 and 300 micrometer. To obtain nano-sized organic particles, the sugarcane straw was ground in a jet mill. Particle size was then determined using a particle size analyzer (Malvern Zetasizer 3000, UK). The reported size was about 327.5 nm (Figure 2). The iodine number corresponding to the produced adsorbent was determined according to the procedure established by the Standard Test Method (ASTM standard D4607-94, 2002). The iodine numbers for micrometer and nanometer-sized Sugarcane straw were 417 and 602 mg/g.

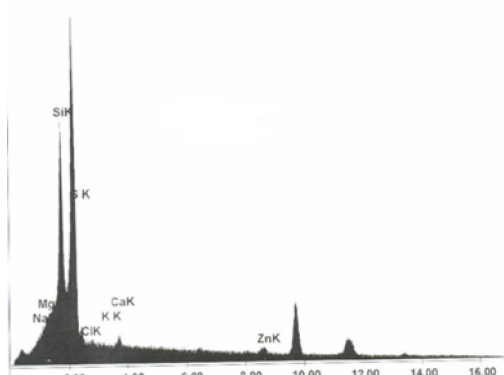
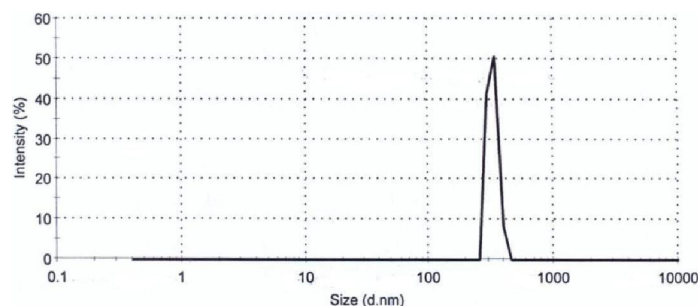


Figure 1. Edax analysis of sugarcane straw particles



	Diam. (nm)	% Intensity	Width (nm)
Peak 1:	327.5	100.0	30.50
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

Figure 2. The particle size distribution of nano-sized sugarcane straw

2.2. Preparation of modified Sugarcane straw- anion exchanger (Sugarcane straw-AE)

In this study, preparation of anion exchangers based on aminated intermediate (epoxypropyl triethylammonium chloride, ETC) was conducted, which comprises first preparation of ETC by reaction of epichlorohydrin with triethylamine, then introduction of ETC into the agricultural by-products in the presence of a catalyst. The synthesis process for sugarcane straw-AE is divided into two steps: At first aminated intermediate was synthesized. An aliquot of 78 ml (1 mol) of epichlorohydrin was reacted with 152 ml (1.1 mol) of triethylamine in 150 ml of 50/50 (v/v) % methanol solution at 55 °C. After stirred for 5h, the produced intermediate was used in the second step. In the second synthesis process, 5g of Sugarcane straw were reacted with 35ml of intermediate and 5ml of pyridine in a 250 ml three-neck round bottom flask for 3h at 55 °C (Xing et al., 2010). The product was washed with distilled water to remove the residual chemicals, dried at 60 °C for 12h then used in all the sorption experiments (Xing et al., 2010). Total nitrogen content of the final

product was determined using a Perker-Elmer Elemental analyzer CHNS/O. Table 1 displays the elemental changes of carbon, hydrogen and nitrogen Sugarcane straw-AE in comparison with Sugarcane straw. The significant increase in nitrogen content (0.67–3.61%) of Sugarcane straw-AE indicates the reactions between Sugarcane straw and aminated intermediate and quite a number of aminated groups have been introduced into the Sugarcane straw-AE. Similar result was observed in the previous work of Xing for the preparation of anion exchangers from wheat straw which have the nitrogen content in the range of 0.35%–3.57% and Gao for the preparation of anion exchangers from coin, rice hull, pure alkaline lignin and sugarcane bagasse, which have the nitrogen contents in the range of 3.6%–5.8% (Gao et al., 2009; Xing et al., 2010). The calculated total exchange capacity (TEC) was based on the nitrogen content incorporated into the final products according to the equation (Laszlo, 1996):

$$TEC(\text{meqg}^{-1}) = \frac{N\%}{1.4} \quad (1)$$

Table 1. Elemental change in sugarcane straw and sugarcane straw-AE

adsorbent	C%	H%	N%	TEC
Sugarcane straw	28.33	3.78	0.67	0.48
Sugarcane straw -AE	34.9	5.25	3.61	2.58

2.3. Chemicals

The 15mg/L of nitrate stock solutions were prepared by dissolving required weighed quantities (24.46mg) of KNO₃ in distilled water. All solutions for sorption and analysis were prepared by appropriate dilution of the freshly prepared stock solution. Sugarcane straw-AE by product represents a potential alternative as an anion exchanger because of its particular properties such as its chemical stability and high reactivity, resulting from the presence of reactive aminated groups in polymer chains. For each 30ml centrifuge tube, 0.3g sugarcane straw-AE and 30ml of working solution was mixed for 3h at 120 rpm. The mixtures were then centrifuged and filtered using filter paper to separate the water from the adsorbent, and then the NO₃⁻ was analyzed by a UV-Vis spectrophotometer (Hach model, DR5000). All samples were prepared in triplicate. The NO₃⁻ exchanged on sugarcane straw- AE was calculated using the equation:

$$q_e = \frac{C_i - C_e}{m} \times V \quad (2)$$

Where q_e is the NO₃⁻ exchanged on sugarcane straw-AE (mg/g), m is the adsorbent mass (g), C₀ and C_e are the initial and equilibrium concentrations of NO₃⁻ in solution (mg/L), respectively, and V is the volume of the solution (L). The removal efficiency was evaluated according to:

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

Where R is the nitrate removal efficiency expressed in %.

2.3.1. Effect of pH

The pH of the KNO₃ solutions (15 mg/L NO₃⁻) were adjusted to different values between 2 and 10 and regulated by using H₂SO₄ or NaOH (0.1N). 0.3g of dried adsorbent was added to solution. After adsorption, the pH value providing the maximum nitrate removal was determined.

2.3.2. Effect of contact time

In kinetic studies, 30 ml KNO₃ solution and 0.3g adsorbent was agitated. The mixtures were shaken at 120 rpm. Batch experiments were repeated for different periods between 10 to 210 minutes until reaching the adsorption equilibrium.

2.3.3. Effect of adsorbent dosage

Adsorption of 15mg/L of NO₃⁻ solution by different adsorbent doses (0.1–1.0g) for adsorbent was carried out at the optimum pH and equilibrium time.

2.3.4. Effect of initial concentration

The effect of initial concentration on the adsorption of NO₃⁻ ions by adsorbent with varying solution concentrations (5, 15, 50, 80, and 120 mg/L) at optimum pH, time and adsorbent dosage was investigated.

2.4. Equilibrium adsorption isotherm

Equilibrium adsorption data were analyzed using different isotherm models to understand the adsorbate–adsorbent interaction. To characterize the exchange equilibrium of NO₃⁻ ions by Sugarcane straw-AE, the Freundlich, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models were used as follows (Malekian et al., 2011):

$$\text{Freundlich equation: } q_e = KC_e^{1/n} \quad (4)$$

$$\text{Langmuir equation: } q_e = \frac{bq_m C_e}{(1 + bC_e)} \quad (5)$$

Redlich_Peterson equation:

$$q_e = \frac{aC_e}{(1 + bC_e^n)} \quad (6)$$

Langmuir_Freundlich equation:

$$q_e = \frac{bq_m C_e^{1/n}}{(1 + bC_e^{1/n})} \quad (7)$$

Where q_e is the nitrate exchanged at equilibrium (mgNO₃⁻/g) and C_e is the nitrate equilibrium concentration in solution (mgNO₃⁻/L). The other parameters represent different isotherm constants that can be determined by regression of the experimental isotherm data. It has been reported that nonlinear regression analysis method is a better method of obtaining the parameters involved in three parameter isotherms (Kumar and Sivanesan, 2006). Therefore, the ion-exchange isotherms were examined by a non-linear curve fitting analysis method, using Data-fit software (<http://www.oakdaleengr.com/datafit.htm>).

Previous studies have shown that commonly used correlation measures such as the correlation coefficient (R) and coefficient of determination (R²) are often unsuitable or confusing when used to compare model estimated

and measured data. Difference measures such as the Root mean square error (RMSE), however, contain insightful information. In this work, the goodness of fit between experimental and model-estimated data was evaluated using R^2 and the RMSE as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (q_e - q_c)^2}{n}} \quad (8)$$

Where q_e and q_c are the measured and model estimated amounts of NO_3^- exchanged, respectively, and n is the number of measurements. A lower RMSE value and higher R^2 value are regard to show goodness of agreement between measured and estimated NO_3^- exchanged data.

2.5. Kinetic study

The rate of adsorption of nitrate was studied at different time intervals that were as long as 210 min using different initial concentrations 5, 15, 50, 80 and 120 mg/L at optimum pH. The modeling of the kinetics of adsorption of NO_3^- on sugarcane straw-AE was investigated by three common models, Eqs. (9)– (12), as described in the later part (Shirvani et al., 2007):

Pseudo first _ orderequation:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (9)$$

Pseudo second _ order equation:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (10)$$

$$\text{Powerequation: } q_t = at^b \quad (11)$$

Elovich equation:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \quad (12)$$

Where q_t is the amount of nitrate removed at time t (mgNO_3^-/g), q_e is the amount of nitrate removed at equilibrium (mgNO_3^-/g), and k_1 , k_2 , , , a , and b are constants.

2.6. Effect of coexisting ions

Coexisting ions such as phosphate (1.5mg/L), nitrate (87mg/L), sulphate (14mg/L), chloride (70mg/L) and bicarbonate (366mg/L) were present in well water. The effect of present ions in well water on nitrate removal by sugarcane straw-AE was investigated

2.7. Desorption studies

After adsorption experiments, after separate the solution from the absorbent, desorption studies of the adsorbed nitrate were carried out by shaking the spent modified sugarcane straw-AE in 30 ml of

0.1 mol/L HCl for a period of 3h. After time passed, the sorbent was filtered and desorbed nitrate concentration was analyzed by UV-Vis spectrophotometer (Hach model, DR5000). The percentage of desorbed (D) nitrate anion was calculated as:

$$\text{Desorption(\%)} = \frac{\text{desorbedamountofsolute}}{\text{absorbedamountofsolute}} \times 100 \quad (13)$$

2.8. Column experiment

Sorption in a continuous-flow system was done in a fixed bed column reactor (2.8 cm i.d., 35 cm column length). Top and bottom of bed of sorbent was filter (40 micron diameter). The column consisted of sugarcane straw-AE. The feed water used was making water, spiked with KNO_3^- , having an initial concentration of 15, 50 and 120 mg/L nitrate. Once the column was saturated with water, there was no visual evidence for air pockets remaining inside the column. The water was pumped upwards into the column using a peristaltic pump at 0.98 L/hr flow rate. Samples were collected from the exit of the column at different time intervals 30 minutes and analyzed for nitrate.

3. Results and discussion

3.1. Adsorption studies

3.1.1. Effect of initial pH

Figure 3 shows the variation in the amount adsorbed as a function of initial pH for nitrate anion. With pH of the solution varying from 2 to 10, $R\%$ and q_e of micrometer sized sugarcane straw-AE increased up to maximum of 56% to 69% and 1.12 to 1.38 mg/g reached at $\text{pH}= 6$, respectively. For nanometer sized sugarcane straw-AE, $R\%$ and q_e increased up to maximum of 45% to 90% and 0.9 to 1.57 mg/g reached at $\text{pH}= 6$, respectively which the adsorbent are positively charged, also enhancement of nitrate adsorption by sugarcane straw-AE as a result of increased electrostatic interactions between sugarcane straw negatively charged nitrate group and positively charged aminated group. Then for $\text{pH}>6$ adsorption performances reaching a constant. Thus, the optimal pH of nitrate removal is 6.0. The adsorption dependence on pH showing ion exchange mechanism (Ulmanu et al., 2008).

3.1.2. Effect of contact time

Figure 4 shows the variation in the amount adsorbed as a function of time for nitrate anion. With varying time from 10 to 210 minutes, $R\%$ and q_e of micrometer sized sugarcane straw-AE increased up to maximum of 27% to 75% and 0.405 to 1.125 mg/g reached at 3h respectively, and for nanometer sized sugarcane straw-AE, $R\%$ and q_e increased up to maximum of 35% to 82% and 0.525 to 1.23 mg/g reached at 2h respectively.

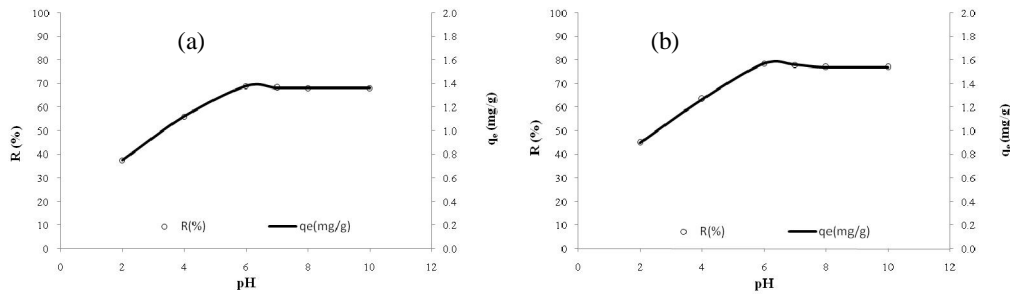


Figure 3. Effect of pH on the adsorption of NO_3^- ion by sugarcane straw-AE (a) micrometer-sized (b) nanometer-sized adsorbent (anion initial concentration: 15mg/L, adsorbent loading: 0.3g, adsorption time: 3h).

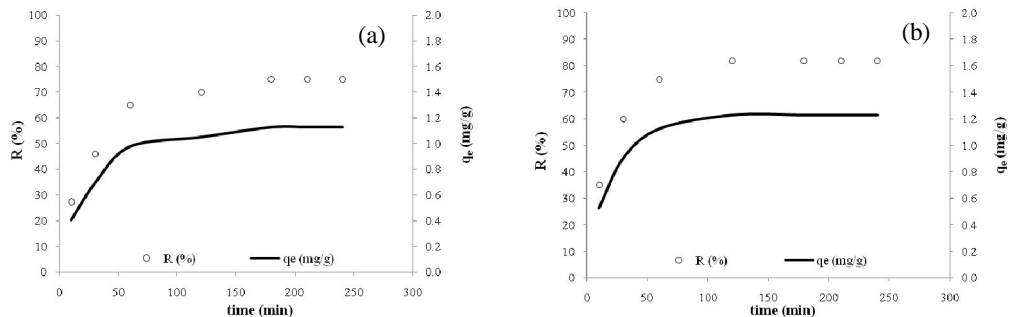


Figure 4. Effect of contact time on the adsorption of NO_3^- ion by sugarcane straw-AE adsorbent (a) micrometer-sized (b) nanometer-sized (anion initial concentration: 15mg/L, adsorbent loading: 0.3g, pH=6).

3.1.3. Effect of adsorbent dosage

For micrometer and nanometer-sized sugarcane straw-AE, with an increase in the adsorbent dosage from 0.1 to 0.5 g, the R% increased from 43% to 69% and 52% to 71% which reached maximum 69% and 71% at 0.5g adsorbent respectively, but remained almost unchanged when adsorbent dosage ranged from 0.5 to 1 g (Figure 5). In general, increase in adsorbent dosage, increased

the percent removal and adsorption capacity of nitrate, which is due to the increase in adsorbent surface area and more adsorption sites. A result that is supported by the findings of Tehrani-Bagha et al., 2011. At adsorbent dosage $>0.5\text{g}$, the extra NO_3^- ion removal becomes very low. Thus, increased adsorbent dosage did not enhance the removal percentage of NO_3^- ion (Tehrani-Bagha et al., 2011).

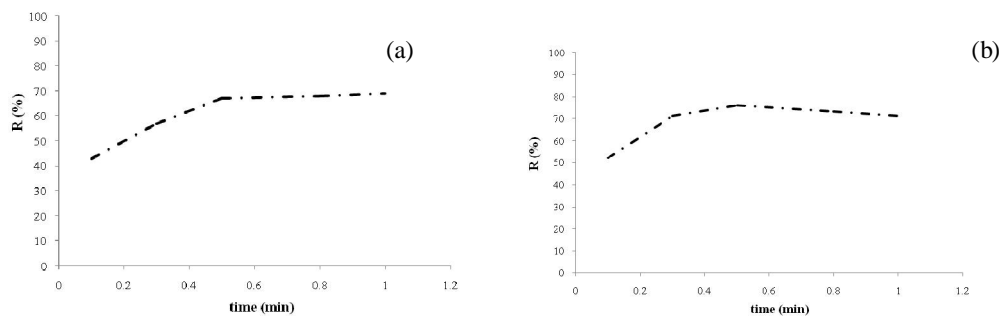


Figure 5. Effect of adsorbent dosage on removal of nitrate by sugarcane straw -AE (a) micrometer-sized (b) nanometer-sized (anion initial concentration 15mg/L, pH=6)

3.1.4. Effect of initial concentration

The effect of initial concentration on the adsorption of NO_3^- ions by sugarcane straw-AE with varying solution concentrations 5, 15, 50, 80, and 120 mg/L using 0.5g adsorbent dose was investigated (Figure 6). With increasing concentration of solution, for micrometer and nanometer-sized sugarcane straw-AE, q_e from 0.39 to 7.24 mg/g and 0.43 to 8.44 mg/g increased respectively, while R% from 78% to 60% and 87% to 80% decreased respectively. At low initial solution concentration, the surface area and the

availability of adsorption sites were relatively high, and the NO_3^- ions were easily adsorbed and removed. The initial high rate of nitrate uptake is probably due to the greater availability of binding sites near the surface of the sugarcane straw-AE adsorbent. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of NO_3^- ions. The increased q_e at higher initial concentration can be attributed to enhanced driving force.

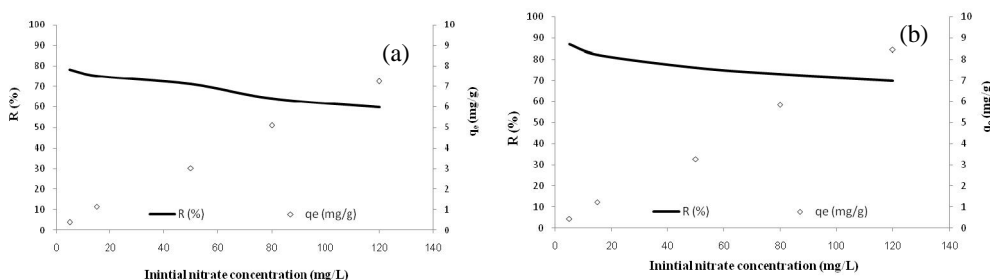


Figure 6. Effect of initial concentration on the removal and adsorption of NO_3^- ions by sugarcane straw-AE (a) micrometer-sized (b) nanometer-sized (adsorbent loading 0.5 g, pH=6)

3.2. Nitrate exchange isotherms

Ion-exchange isotherms characterize the equilibrium relationship between the amounts of exchanged ion by sugarcane straw-AE and its equilibrium concentration in the solution (19). In this work, the ion exchange isotherm data obtained for micrometer and nanometer sized sugarcane straw-AE were fitted to the Freundlich, Langmuir, Redlich–Peterson, and Langmuir–Freundlich models. The resulting exchange isotherms as well as experimental data are shown in Figure 7. The estimated model parameters, including R^2 and the RMSE, for the different models are presented in Table 2, which indicates that the experimental data

of NO_3^- exchange could be well fitted by all four models. It was also made clear that the three-parameter models (Langmuir–Freundlich) provided better fitting in terms of R^2 and RMSE for all treatments compared to two-parameter isotherms (Freundlich and Langmuir), a result that is supported by the findings of Malekian et al., 2011. In practice, however, two-parameter equations are more extensively used than three parameter equations due to the difficulty of analyze three parameters isotherm. For two-parameter isotherms, the Langmuir model provided a more conforming to the experimental data compared with the Freundlich model (Table 2).

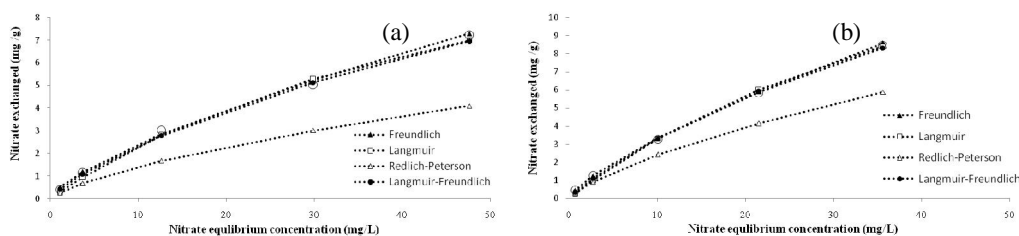


Figure 7. NO_3^- exchange isotherms by Sugarcane straw-AE (a) micrometer-sized (b) nanometer-sized

Table 2. Isotherm constants and statistical comparison values for NO₃⁻ exchange from solutions on micrometer and nanometer- sized sugarcane straw-AE

Model	Micrometer-sizes	Nanometer-sizes
Freundlich		
k	0.47	0.59
1/n	0.71	0.75
R ²	0.98	0.978
RMSE	0.244	0.369
Langmuir		
q _m (mg/g)	15.17	21.56
b (L/mg)	0.018	0.018
R ²	0.994	0.987
RMSE	0.214	0.351
Redlich-Peterson		
a	0.412	0.788
b	0.7	0.9
n	0.436	0.401
R ²	0.997	0.999
RMSE	1.779	1.43
Longmuir - Freundlich		
q _m (mg/ g)	30	32
b(Lm/g)	0.013	0.015
1/n	0.81	0.88
R ²	0.997	0.999
RMSE	0.174	0.091

The dimensionless parameter or separation factor, R_L , based on the more analysis of the Langmuir equation can be given by (Saltali et al., 2007):

$$R_L = \frac{1}{1 + bC_0} \quad (14)$$

Where C_0 (mg/L) is the initial concentration of exchangeable ion and b is the Langmuir constant. The R_L parameter is considered as more valid indicator of exchange.

There are four possibilities for the R_L value: (i) for favorable exchange, $0 < R_L < 1$, (ii) for unfavorable exchange, $R_L > 1$, (iii) for linear exchange, $R_L = 1$, and (iv) for irreversible exchange, $R_L = 0$ (16). Figure 8 illustrates the variation of R_L with initial concentration of the NO₃⁻ ion for all treatments. As can be seen from the fig.8, the R_L parameters are to be found between 0 and 1 which indicates that the removal of NO₃⁻ ions by sugarcane straw-AE is suitable. The R_L value obtained also demonstrate that sugarcane straw-AE is a potential ion-exchanger for NO₃⁻ ion removal from aqueous solutions, which is supported by several previous studies (Malekian et al., 2011; Saltali et al., 2007). Figure 8 also shows that the R_L value approaches zero as the C_0 value is increased, which indicates that the exchange of NO₃⁻ ion onto

sugarcane straw- AE is less favorable at high concentrations of NO₃⁻ (Saltali et al., 2007).

Another parameter, q_m , used in either the Langmuir or Langmuir–Freundlich equations, represents the NO₃⁻ ion-exchange capacity (Lei et al., 2008) and is presented in Table 2 for micrometer and nanometer-sized sugarcane straw-AE. It is believed that q_m obtained from the Langmuir–Freundlich equation can be more reasonable than from the Langmuir equation (Lei et al., 2008). The comparison of q_m for micrometer and nanometer-sizes Sugarcane straw- AE suggests that the maximum NO₃⁻ exchange increases with decreasing particle size (Table 2), a result that is consistent with Malekian et al., 2011. The maximum NO₃⁻ exchange capacity by the sugarcane straw at equilibrium was 30 and 32 mgNO₃⁻/g for micrometer and nanometer-sized sugarcane straw-AE, respectively (Table 2). The 1/n constant for the Freundlich isotherm ranges from 0 to 1 and is a measure of exchange intensity or surface heterogeneity, with a value of 1/n smaller than 1 describing a favorable removal conditions (Raji and Anirudhan., 1998). In this study, the value of 1/n (Freundlich constant) for sugarcane straw-AE was between 0.81 and 0.88 (Table 2), which suggests that the exchange conditions were actually favorable.

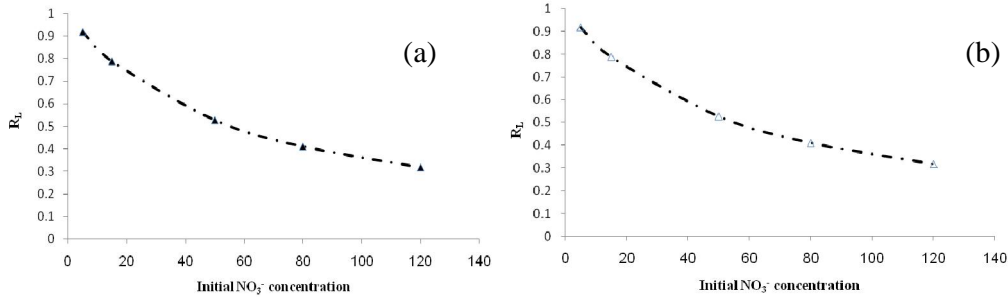


Figure 8. Variation of separation factor (R_L) as a function of initial NO_3^- concentration for sugarcane straw-AE of micrometer-sized (a) and nanometer- sized (b)

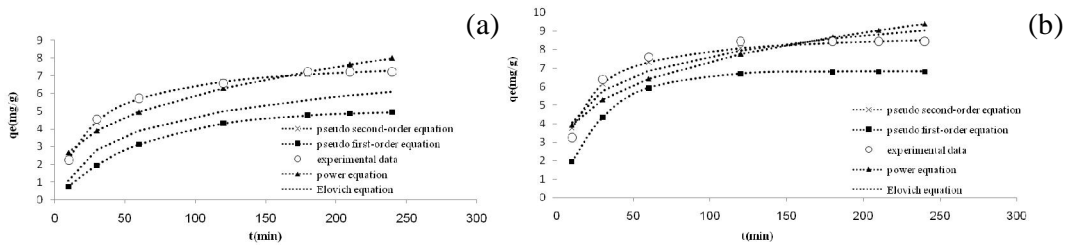


Figure 9. The fitting of kinetic models for NO_3^- on sugarcane straw for 120 mg/L initial concentration (a) micrometer-sized (b) nanometer- sized

Table 3. Kinetic models parameters for the adsorption of NO_3^- on sugarcane straw and 120 mg/L initial NO_3^- concentration (C_0 : mg/L; q_e : mg/g; k_1 : min^{-1} ; k_2 : g/mg min, a : mg/g min and b : g/mg)

Model	Micrometer-sized	Nanometer-sized
Pseudo first _ order equation		
q_{exp}	7.24	8.439
k_1	0.016	0.034
q_e	5.05	6.82
R^2	0.97	0.98
RMSE	2.34	2.904
Pseudo second_ order equation		
K_2	0.005	0.008
q_e	8.06	9
R^2	0.99	0.99
RMSE	0.097	0.285
Power function		
a	1.2	2.09
b	0.342	0.274
R^2	0.94	0.84
RMSE	2.3	0.752
Elovich equation		
$\frac{1}{\beta} \ln(\alpha\beta)$	-1.52	0.44
$\frac{1}{\beta}$	1.569	1.568
R^2	0.97	0.9
RMSE	1.52	0.555

3.3. Kinetic study

The fittings of the experimental kinetic results to the four models are shown in Figure 9 and the estimated parameters values are presented in Table 3. It can be seen for micrometer and nanometer-sized sugarcane straw, the R^2 values for pseudo-second-order model gives the best fit R^2 : 0.99, 0.99 and RMSE: 0.097, 285 but its predicted q_e values 8.06, 9 mg/g are overestimated as compared to the experimentally observed values (7.24mg/g). In pseudo-first-order, predicted q_e values 5.05, 6.82 mg/g were lower than experimentally observed values (7.24mg/g). However, q_e values estimated from the pseudo-second-order model are an extrapolation outside the time period that was experimentally investigated, the fact still remains that the model accurately predicts the adsorption kinetics throughout the period of experiments. The higher RMSE values obtained for the pseudo first-order were 2.34 and 2.904 respectively. Therefore, the pseudo-second-order model could be used for the prediction of the kinetics of adsorption of NO_3^- on sugarcane straw-AE.

The Power function model satisfactorily describes the NO_3^- removed by micrometer and nanometer-sized sugarcane straw-AE with RMSE: 2.3, 0.752, R^2 : 0.94, 0.84, respectively (Table 3). The elovich model describes the NO_3^- removed by micrometer- sizes and nanometer-sizes sugarcane straw with RMSE: 1.52, 0.555 and R^2 : 0.97, 0.9, respectively (Table 3). The results showed that the pseudo-first-order rate expression was not valid in the present systems studied (Table 3). The calculated and experimental equilibrium uptake value fit well to pseudo-second-order rate model which indicates that the pseudo second order reaction is better than pseudo-first-order reaction.

Among micrometer and nanometer-sized sugarcane straw, nanometer particle size was fine, spherical, high surface area, has high activity and adsorb ion quickly which same result obtained by Rahmani et al., 2010 (Rahmani et al., 2010). It was found that the fitting to pseudo-second-order model gave the highest values of determination coefficients (R^2), lowest RMSE and predicted q_e more accurately than the other models investigated. Therefore, pseudo-second-order model could be used for the prediction of the kinetics of adsorption of NO_3^- on the adsorbent (Ozturk and Ennil Kose., 2008).

3.4. Effect of coexisting ions

Figure 10 shows the influence of coexisting ions on the adsorption of studied ion. The experiments were conducted with mixtures containing nitrate, sulphate, phosphate, chloride and bicarbonate. Presence of high concentrations of bicarbonate (366mg/L) and chloride (70mg/L) has obvious effect on the studied nitrate ion adsorption under reported conditions. The same result obtained by Samatya et al., 2006 (Samatya et al., 2008). Initial concentration of SO_4^{2-} , and PO_4^{3-} ions were less than NO_3^- ion. Therefore the presence of SO_4^{2-} and PO_4^{3-} ions did not disturb the adsorption significantly. The R% for NO_3^- , Cl^- and HCO_3^- ions for micrometer-sizes and nanometer-sizes sugarcane straw-AE obtained 59.01%, 8.57%, 56.28% and 62.49%, 21.43%, 72.68%, respectively. The results showed that interactions between nitrate ions and other ions on sugarcane straw-AE are hindered in the presence of chloride and bicarbonate ions (bicarbonate especially).

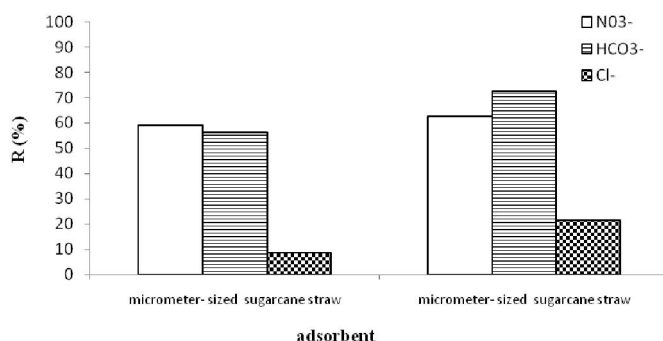


Figure 10. The effect of coexisting ions on nitrate removal by sugarcane straw-AE

3.5. Desorption

The results relating to desorption of NO_3^- by HCl are shown in table 4. The results showed that HCl demonstrate the high desorption capacities;

this indicate that, the reverse of the reactions with Cl^- from the HCl solution displacing NO_3^- ion onto sugarcane straw-AE adsorbent.

Table 4: Desorption parameters of desorption solvent

Adsorbent	Adsorbed nitrate (mg/L)	Desorbed nitrate (mg/L)	Desorption efficiency (%)
micrometer-sized sugarcane straw	11.3	7.16	63.36
Nanometer-sized sugarcane straw	12.3	9.12	74.15

4. Result of column experiment

Figure 11 shows the variation in the equilibrium nitrate concentration as a function of

time on micrometer and nanometer-sized sugarcane straw-AE.

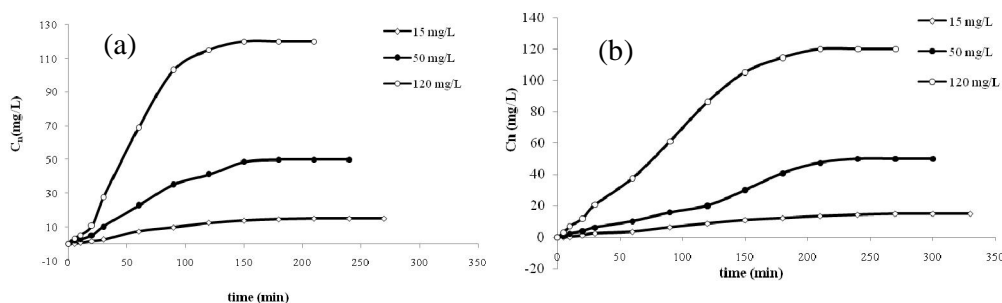


Figure 11. The change of equilibrium nitrate concentration with time on sugarcane straw-AE (a) micrometer-sized (b) nanometer-sized (flow rate: 0.98L/h, initial concentration of nitrate: 15, 50 and 120 mg/L, pH=6)

For micrometer-sized with flow rate of 0.98 L/hr, exhaustion time and adsorption capacity (q_e) obtained at 180, 150, 120 min and 3.84, 11.57, 24.54mg/g for 15, 50 and 120 mg/L initial nitrate concentration, respectively. For nanometer-sized sugarcane straw-AE, exhaustion time obtained at 240, 210, 180 min and 6.99, 12.7, 17.28 mg/g for 15, 50 and 120 mg/L initial nitrate concentration respectively (Figure 11). As indicated in Figure 11 at higher initial concentration of nitrate, a relatively higher uptake value was observed for nitrate sorption on sugarcane straw-AE. A higher q_e is observed at higher concentrations in column test for nitrate removal that attribute to the concentration gradient which will enhance the adsorption process. Similar results were reported in the work of Xing for the nitrate and phosphate removal by WS-AE and Han's work for methylene blue adsorption onto natural zeolite in fixed-bed column (Han et al., 2007; Xing et al., 2010). The exhaustion time decreased with increasing initial concentration of nitrate. This behavior due to with increasing initial concentration, sites of adsorbent filled quickly.

5. Conclusion

In this study, the examined experimental parameters, such as pH, adsorbent dosage, initial NO_3^- concentration, coexisting ions and sugarcane straw particle size, influenced the removal of NO_3^- ion by sugarcane straw-AE. The nitrate removal was optimal at pH= 6, and 180, 120 minutes equilibrium time in batch experiments for micrometer and nanometer-sized sugarcane straw-AE. Higher initial nitrate concentrations led to lower removal percentages but higher adsorption capacity. As the adsorbent dose increased, the removal of nitrate increased, while the adsorption capacity decreased. The NO_3^- ion exchange capacity of sugarcane straw-AE increased with decreasing particle size, and the NO_3^- ion exchange data was fitted to the Freundlich, Langmuir, Redlich-Peterson, and Langmuir-Freundlich models. Adsorption kinetics of nitrate ions onto sugarcane straw-AE could be most successfully described by the pseudo-second order kinetic model. The exhaustion time and total adsorbed nitrate quantity increased with increasing initial nitrate concentration of the solute in the adsorption column. Based on the results, it can be concluded

that sugarcane straw-AE is a suitable anion-exchanger for NO_3^- removal and it can be recommended for use in wastewater treatment and agriculture purposes as it represents a sustainable and affordable ion exchange material. Because of develop high capacity and selective of nanoparticles for nitrate removal, nanometer-sized sugarcane straw-AE had higher ability of nitrate adsorption than micrometer-sized sugarcane straw-AE.

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