A Kinetic Study of Nitrite Adsorption onto Modified Phragmites and Sugarcane Straw

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Abstract: In this research, removal of nitrite from aqueous solution by selective ion exchange phragmites australis and sugarcane straw was investigated. In order to investigate the adsorption mechanisms, five kinetic models, pseudo-first-order, pseudo-second-order, intraparticle diffusion, the power and elowich models were applied to fit the kinetic data obtained from experiment by using phragmites australis and sugarcane straw adsorbents. The rate constants for the five models were determined and the correlation coefficients were calculated. Adsorption followed pseudo-second-order rate kinetics for all adsorbents. Adsorption kinetics of nitrite ions onto modified phragmites australis and sugarcane straw could be most successfully described by the pseudo-second order kinetic model with higher R² (0.993-0.997) and lower RMSE (0.134-0.332). Also because of unique properties of nanoparticles to develop high capacity and selective sorbents for removal of anions, nanostructure adsorbents had higher ability of nitrate adsorption than microstructure adsorbents.

Key word: Phragmites australis • Sugarcane straw • Nitrate removal • Aqueous solution • Nanostructure adsorbent

INTRODUCTION

Nitrate contamination in the environment can create serious problems, such as eutrophication of rivers and possible hazard on human health. High concentrations of nitrate in drinking water cause health problems such as cancer and increase the risk of diseases such as blue baby in new born infants [1, 2]. There are various techniques for nitrate removal from contaminated water such as denitrification, nitrification, chemical coagulation, adsorption, selective ion exchange, ammonia stripping, electrodialysis, filtration and reverse osmosis [3-6]. The ion exchange process seems to be the most appropriate for water contaminated by nitrate because of its ease of application, usefulness, selectivity, recovery and relatively low cost [6, 7].

Recently, many attempts have been made in finding economical and effective anion exchangers produced in agricultural by-products. Some studies showed that many materials such as sugarcane bagasse, coconut husk and wheat straw could be modified into anion exchangers and utilized for this purpose [8-11]. The reuse of industrial wastes in the agriculture segment is increasingly encouraged, principally in developing countries. All agricultural residues are biological forms of renewable energy. It was already known [12] that sugar cane straw (sugar cane leaves) can be recycled in the manufacture of commercial cements and other composites, either as raw material. The sugarcane straw is burnt in open landfills, contributing to air and water pollution. Also, there is a growing shortage of landfills in most countries [13]. Sugarcane growers rely heavily upon multiple and high dosage applications of a small number of herbicides, the majority of which were developed many years ago and utilize only a few modes of action. Phragmites has also been planted in systems constructed for waste treatment [14]. Ethnographic identification of Phragmites is confused by a variety of common names including reed, common reed, reed grass, common reed grass, cane, common cane, wild cane, arrow cane, cane grass, Carrizo, sCarrizo grass, carrizal reed, Roseau and bent grass.

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Some of these names have also been applied to Scirpus, Typha, Acorus, Arundinaria and other taxa. However, for the case of Phragmites australis and sugarcane straw wastes there is an important lack of experimental work [15]. In this study sugarcane straw and phragmites collected from area of Khuzestan province, Alwaz was used as adsorbents for nitrite removal. Phragmites australis and sugarcane straw modified and for nitrate removal investigated. The experimental data were analyzed using the pseudo-first order, pseudo-second order, intraparticle diffusion, power, elovich models and kinetic constants were evaluated. The results are presented and discussed in this study.

Experimental
Preparation of Phragmites Australis and Sugar Cane Straw Anion Exchange: The phragmites australis and sugarcane straw were collected in the area of Khuzestan province, Alwaz. Then the collected material washed with double distilled water and then dried. In this work, preparation of anion exchangers based on amminated intermediate (epoxypropyl triethyammonium chloride, ETC) is conducted, which comprises first preparation of ETC by reaction of epichlorohydrin with triethyamine, then introduction of ETC into the agricultural by-products in the presence of a catalyst. The synthesis process for modify adsorbents is divided into two steps; in the first step amminated intermediate was synthesized. An aliquot of 78 ml (1 mol) of epichlorohydrin was reacted with 152 ml (1.1 mol) of triethyamine in 150 ml of 50/50 (v/v) % methanol solution at 55 °C. After stirred for 5 h, the produced intermediate was used in the second step. In the second synthesis process, 5 g of adsorbent was reacted with 35 ml of intermediate and 5 ml of pyridine in a 250 ml three-neck round bottom flask for 3 h at 55°C [16]. The product was washed with distilled water to remove the residual chemicals materials, dried at 60 °C for 12 h and sieved to obtain particles with microstructure and nanostructure scales then used in all the sorption experiments [16].

Characteristics of Adsorbent: To examine the surface of the four adsorbents, a scanning electron microscope (SEM) was used the iodine number and adsorption test of methylene blue on modified adsorbents was determined [17, 18].

Chemical analysis results of phragmites australis and sugar cane straw that obtained by using Edax analysis is given in Table 1.

METHODS

Adsorption Studies: Adsorption of nitrate ions by phragmites australis and sugarcane straw was studied by batch experiments. Stock solution of NO₃⁻ was prepared by dissolving KNO₃ in distilled water having 120 mg/L of NO₃⁻. A fixed amount of dry adsorbents (0.3 g) and 30 mL of KNO₃ solution were put in capped volumetric flask and shaken at 120 rpm. After centrifuging of adsorption samples (5000 rpm with 30 min), they was filtered using Whatman 42 filter paper to separate the water from the absorbent and the filtrate was analyzed in a UV-Vis spectrophotometer (model Hach, DR5000).

Kinetic Studies: In kinetic studies, 30 mL KNO₃ solution and 0.3g of adsorbent was agitated. The mixtures were shaken at 120 rpm. Batch experiments were repeated for different periods between 5 to 210 minutes until reaching the adsorption equilibrium. All the results obtained in the experiments were corrected from blanks performed under the same conditions but in the absence of sorbents species.

RESULTS AND DISCUSSION

Particle size of phragmites australis adsorbent used in adsorption experiments is shown in Figure 1-2. Particle size of phragmites australis adsorbent between (125-330 μm) and (18.5% of particles diameter less than 51.47 nanometer and 81.5% of particles diameter less than 406 nanometer). Particle size of sugarcane straw were between (125-330 μm) and (particles diameter less than 327.5 nanometer). Characteristics of adsorbents prepared were evaluated (Figure 3). It was observed that number of ammonium group was graft in the structure of phragmites australis and sugarcane straw. Based on the characteristics of modified adsorbents mentioned above, it is evident that the grafted functional groups in modified adsorbents would be beneficial for the sorption of nitrate ions from solution. Pyridine was used as a weak-base catalyst to open the strained three-membered...
Fig. 1: The particle size distribution of nano-sized phragmites australis adsorbent

![Graph showing particle size distribution.]

<table>
<thead>
<tr>
<th>Diam. (nm)</th>
<th>% Intensity</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1:</td>
<td>405.0</td>
<td>81.5</td>
</tr>
<tr>
<td>Peak 2:</td>
<td>51.47</td>
<td>360.09</td>
</tr>
<tr>
<td>Peak 3:</td>
<td>600.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Fig. 2: The particle size distribution of nano-sized sugarcane straw adsorbent

![Graph showing particle size distribution.]

<table>
<thead>
<tr>
<th>Diam. (nm)</th>
<th>% Intensity</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1:</td>
<td>327.5</td>
<td>100.0</td>
</tr>
<tr>
<td>Peak 2:</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Peak 3:</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Fig. 3: Synthetic reactions of adsorbents anion-exchanger.

![Chemical diagrams showing synthetic reactions.]

Table 2: Physical characteristics of adsorbents

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>Surface area</th>
<th>Iodine number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phragmites australis-micro</td>
<td>23.5</td>
<td>430</td>
</tr>
<tr>
<td>Phragmites australis-nanostructure</td>
<td>45</td>
<td>665</td>
</tr>
<tr>
<td>Sugar cane straw-micro</td>
<td>18</td>
<td>417</td>
</tr>
<tr>
<td>Sugar cane straw-nanostructure</td>
<td>39</td>
<td>602</td>
</tr>
</tbody>
</table>

ring of the epoxide group in base conditions [8, 16]. Table 2. Showed Physical characteristics of adsorbents. The result of table 2 showed that Phragmites australis-nanostructure have high surface area and iodine number which corresponding to fine particles and more pores in structure of it.

Figure 4-7, shows the SEM Photographs of microstructure and nanostructure phragmites australis and sugar cane straw before and after modification.

By considering fig.4. after modify, phragmites australis has honey comb voids and more pores [19] and look rougher which indicated increasing in the surface area of adsorbent. The surface of modified nanostructure phragmites is softer and smoother (Figure 5) which imply on the high nitrate adsorption on the adsorbent [20-22].

Fig. 6. Shows the SEM Photographs of microstructure sugar cane straw, the fractured and observed fragmented walls of the pores, the same results obtained by Namasivayam and Sangeetha [19].

For nanostructure sugarcane straw, it was found that the surface of sugarcane straw after modify smoother and had many holes that explained this phenomenon as heterogeneous energy distribution of the activated adsorption sites on microstructure sugarcane straw surface. It is observed that nanoparticles trend to aggregate, that cause increase of their size and this factor dependent on adsorbent dosage. The modified nanostructure adsorbents contained relatively large surface area and total pore volume compared to modified microstructure adsorbents.
Fig. 4: SEM Photographs of microstructure phragmites australis (a) before modified (b) after modified

Fig. 5: SEM Photographs of nanostructure phragmites australis (a) before modified (b) after modified

Fig. 6: SEM Photographs of microstructure sugar cane straw (a) before modified (b) after modified

Fig. 7: SEM Photographs of nanostructure sugar cane straw (a) before modified (b) after modified

**3Effect of Contact Time:** Effects of contact time on removal of nitrite by several adsorbents are shown in Figure 8. The values of equilibrium time were found to be 120 min for nanostructure adsorbents, 180 min for micro adsorbents. By considering Figure 8, the removal of nitrite is rapid in the initial stages of contact time and slowly increases with lapse of time until saturation. The value of nitrate removal for all adsorbents is given table 3. The removal efficiency of micro and nanostructure phragmites australis and sugar cane straw were 78%, 86%, 75% and
Fig. 8: Effect of contact time on the removal of nitrite by micro and nanostructure phragmites australis and sugar cane straw.

Table 3: Nitrate removal efficiency of adsorbents (0.3g adsorbent in 30 ml solution)

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>equilibrium time</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phragmites australis-micro</td>
<td>180</td>
<td>78</td>
</tr>
<tr>
<td>phragmites australis-nano</td>
<td>120</td>
<td>86</td>
</tr>
<tr>
<td>sugar cane straw-micro</td>
<td>180</td>
<td>75</td>
</tr>
<tr>
<td>sugar cane straw-nano</td>
<td>120</td>
<td>82</td>
</tr>
</tbody>
</table>

82% respectively. The removal efficiency of phragmites australis was more than sugarcane straw that due to its has honey comb voids and more pores than sugarcane straw. Also the removal efficiency of nanostructure phragmites australis (86%) is more than other adsorbents which probably due to nanoparticles and nanostructure available in nanostructure phragmites australis and higher specific surface area and activity.

**Adsorption Kinetics:** Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores. In order to study the controlling mechanisms of the adsorption process, the pseudo-first-order, pseudo-second-order, intra particle diffusion, power and elovich models were used to test the experimental data. The amount of nitrate removal was described by Eqs. (1)-(4), as described in the later part [23]:

**Pseudo First-Order Equation:** The rate constant of adsorption is determined by the following first-order rate expression that is given by Lagergreen [24]:

\[ q_t = q_e(1-e^{-kt}) \]  \( (1) \)

Where \( q_t \) and \( q_e \) are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively and \( k \) (1/min) is the rate constant of first-order adsorption.

A linear form of pseudo-first order model is:

\[ \log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \]  \( (2) \)

**Pseudo Second-Order Equation:** A second-order equation based on adsorption equilibrium capacity may be expressed in the form [25]:

\[ \frac{t}{q_t} = \frac{1}{k_q q_e^2} + \frac{t}{q_e} \]  \( (3) \)

Where \( q_t \) and \( q_e \) are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time \( t \) (min) and \( k \) (g/(min mg)) is the rate constant of second-order adsorption.

A linear form of pseudo-second order model, Ho and MaKay's pseudo-second order model is as follows:

\[ \frac{t}{q_t} = \frac{1}{k_q q_e^2} + \frac{t}{q_e} \]  \( (4) \)

**Elovich Model:** Elovich model is expressed in the form [26]:

\[ \frac{t}{q_t} = \frac{1}{k_q q_e^2} + \frac{t}{q_e} \]  \( (5) \)
Elovich equation:

\[ q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t \]  

(5)

Where \( q_t \) is the amount of nitrate removed at time \( t \) (mg/g), \( \alpha \) is the initial adsorption rate (mg/g min) and \( \beta \) is the desorption constant (g/mg).

**Intraparticle Diffusion Model:** Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulate, followed by diffusion of the solute molecules into the pore interiors [27]. The intraparticle diffusion equation can be described as:

\[ q_t = k t^{1/2} + c \]  

(6)

Where \( k \) is intraparticle diffusion rate constant (mg/g min\(^{0.5}\)) and \( c \) is constant. The \( k \) and \( c \) are the slope and intercept of straight line portions of the plot of \( q_t \) vs. \( t^{1/2} \).

**Power Equation:** The Power equation can be described as [26]:

\[ Power\ equation: \ q_t = at^b \]  

(7)

Where \( q_t \) is the amount of nitrate removed at time \( t \) (mg/g), \( a \) and \( b \) are constants.

Previous studies have shown that commonly used correlation measures such as the correlation coefficient (\( R \)) and coefficient of determination (\( R^2 \)) 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 proper and insightful information [28]. Therefore in this study, the goodness of fit between experimental and model-estimated data was evaluated using \( R^2 \) and the RMSE as follows:

\[ RMSE = \sqrt{\frac{\sum (q_m - q_e)^2}{n}} \]  

(8)

Where \( q_m \) and \( q_e \) are the measured and model estimated amounts of NO\(_3\)-exchanged, respectively and \( n \) is the number of measurements.

\( R^2 \) and RMSE for the different models were determined and a lower RMSE value and higher \( R^2 \) value were considered to represent goodness of agreement between the measured and estimated nitrate removed data.

The fittings of the experimental kinetic results to the five models are shown in Figures 9-12 and the estimated parameters values are presented in Table 4.

The lower RMSE (0.134-0.332) and higher \( R^2 \) (0.993-0.997) values obtained with the pseudo second order model suggest that at adsorption kinetics were best fitted to this model (Table 4). Among the models examined, the higher RMSE values obtained for the pseudo first-order model varied between 1.66 and 2.904 (Table 4). The possibility of first-order reactions corresponding to multiple independent retention sites in the adsorbents.

![Graph showing nitrate removal by phragmites australis-micro](image)

Fig. 9: Kinetic data nitrate removal by phragmites australis-micro

1507
Fig. 10: Kinetic data nitrate removal by phragmites australis-nano

Fig. 11: Kinetic data nitrate removal by sugar cane straw-micro

Fig. 12: Kinetic data nitrate removal by sugar cane straw-nano
Table 4: Kinetic models for NO₂-removed from adsorbents

<table>
<thead>
<tr>
<th>models</th>
<th>phragmites australis-micro</th>
<th>phragmites australis-nano</th>
<th>sugar cane straw-micro</th>
<th>sugar cane straw-nano</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_{eq} )</td>
<td>7.68</td>
<td>9.35</td>
<td>7.24</td>
<td>8.439</td>
</tr>
<tr>
<td>( q_0 )</td>
<td>5.87</td>
<td>6.5</td>
<td>5.09</td>
<td>6.82</td>
</tr>
<tr>
<td>( K_1 )</td>
<td>0.023</td>
<td>0.032</td>
<td>0.016</td>
<td>0.034</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.989</td>
<td>0.984</td>
<td>0.968</td>
<td>0.989</td>
</tr>
<tr>
<td>RMSE</td>
<td>1.89</td>
<td>2.904</td>
<td>2.311</td>
<td>1.66</td>
</tr>
<tr>
<td>pseudo second order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_0 )</td>
<td>8.4</td>
<td>9.9</td>
<td>8.06</td>
<td>9</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>0.006</td>
<td>0.01</td>
<td>0.005</td>
<td>0.009</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.996</td>
<td>0.993</td>
<td>0.997</td>
<td>0.986</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.134</td>
<td>0.285</td>
<td>0.097</td>
<td>0.332</td>
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<tr>
<td>Elovich model</td>
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</tr>
<tr>
<td>( \alpha )</td>
<td>1.12</td>
<td>4.02</td>
<td>0.82</td>
<td>2.07</td>
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<tr>
<td>( \beta )</td>
<td>0.65</td>
<td>0.65</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.957</td>
<td>0.901</td>
<td>0.979</td>
<td>0.898</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.366</td>
<td>0.555</td>
<td>0.251</td>
<td>0.573</td>
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<tr>
<td>Power function</td>
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<td></td>
</tr>
<tr>
<td>( a )</td>
<td>1.5</td>
<td>2.92</td>
<td>1.2</td>
<td>2.09</td>
</tr>
<tr>
<td>( b )</td>
<td>0.317</td>
<td>0.228</td>
<td>0.346</td>
<td>0.274</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.89</td>
<td>0.84</td>
<td>0.94</td>
<td>0.84</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.64</td>
<td>0.75</td>
<td>2.35</td>
<td>0.752</td>
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<tr>
<td>Intraparticle model</td>
<td></td>
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<tr>
<td>( k )</td>
<td>0.368</td>
<td>0.348</td>
<td>0.37</td>
<td>0.353</td>
</tr>
<tr>
<td>( c )</td>
<td>2.64</td>
<td>4.684</td>
<td>2.098</td>
<td>3.705</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.84</td>
<td>0.75</td>
<td>0.94</td>
<td>0.75</td>
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<tr>
<td>RMSE</td>
<td>0.71</td>
<td>0.88</td>
<td>2.35</td>
<td>2.64</td>
</tr>
</tbody>
</table>

The Power function model satisfactorily describes the NO₂-removed by the adsorbents with RMSE and \( R^2 \) values ranging from 0.64 to 2.35 and 0.84 to 0.94, respectively (Table 4).

By considering tables 5 and figure 9-12., intraparticle diffusion equation have intercept (2.098-4.684) indicated that plot did not pass through the origin. Suggesting that the intraparticle diffusion was not the sole rate-controlling step of initial adsorption. Therefore adsorption mechanism with intraparticle diffusion rate-controlling step initial adsorption. The intraparticle diffusion model describes the NO₂ removed by the adsorbents with RMSE and \( R^2 \) values ranging from 0.71 to 2.64 and 0.75 to 0.94, respectively (Table 4).

Comparison adsorption capacity \( (q_{eq}) \) of pseudo second order and pseudo first-order showed that for pseudo second order, predicted \( q_e \) values (8.06-9.9) are overestimated as compared to the experimentally observed (7.34-9.25) values. But in pseudo first-order, predicted \( q_0 \) values (5.08-6.82) are lower than experimentally observed (7.34-9.25) values. The results showed that the pseudo-first-order rate expression was not valid in the present systems studied. The experimental \( q_e \) values did not agree with the calculated ones, obtained from the linear plots (Table 4).

The results showed that 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.

The initial adsorption rates \( (K_0q_0^2) \) of pseudo second order for nanostructure phragmites australis more than other adsorbents. In elovich model, \( \alpha \) is the initial adsorption rating that for adsorbents between (0.82-4.02). Among micro and nanostructure adsorbents, nanostructure adsorbents have high \( \alpha \), \( k_0q_0^2 \) and adsorbed NO₂ with more rate than microstructure that corresponding to particle size of adsorbents. Nanostructure adsorbents were fine particles, spherical and high surface area has high activity and adsorb ion quickly which same result obtained by Rahmani et al. [29].
It was found that the fitting to Ho's pseudo-second-order model gave the highest values of determination coefficients (R²) and lowest RMSE and predicted qe more accurately than the other models investigated. Therefore, Ho's pseudo-second-order model could be used for the prediction of the kinetics of adsorption of NO₃⁻ on the adsorbent. The same result obtained by other research [30, 31].

CONCLUSION

In this paper the suitability of the kinetic models for the adsorption of nitrate on the adsorbents was investigated. Adsorption kinetic data were analyzed using the pseudo-first-order, pseudo second order, intraparticle diffusion, power and elovitch model. The results shown the process can be described by a pseudo-second-order model. The advantage of using this model is that the adsorption capacity, the rate constant of pseudo-second-order and the initial adsorption rate at any given time t, can be predicted from the equation. Nanostucture Phragmites australis and sugar cane straw has adsorption properties due to softer and more pores in its structure, high surface area and high sorption capacities. Since nanostucture phragmites australis and sugar cane straw are waste material from hand carving, the treatment method seems to be economic.

REFERENCES