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ISOTHERM AND KINETICS STUDY FOR THE ADSORPTION OF NITRATE FROM AN AQUEOUS SOLUTION USING A MODIFIED RICE STRAW

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ABSTRACT

In this research, modified rice straw (MRS) is proposed. The proposed production process of the modified rice straw (MRS) adsorbent is carried out by precipitation of iron nano particles on the surface of acid activated rice straw. The nitrate adsorption is carried out through batch experiments. The optimum nitrate removal 94.8 % was achieved at Ph = 7, adsorbent dose 3 = g/L, 150 rpm, initial nitrate concentration = 23 mg/L and contact time 180 = min. The new adsorbent synthesis, kinetics and isotherm models were studied. The nitrate adsorption was well described by pseudo second order kinetic model ($R^2 = 0.999$) as it fitted with the experimental results better than the pseudo first order kinetic model ($R^2 = 0.872$). The rate limiting step was determined using intraparticle diffusion model and Byod plot. For two parameters isotherm model; Freundlich and Halsey isotherms ($R^2 = 0.997$) fitted with the experimental results better than Langmuir isotherm model ($R^2 = 0.973$). For three parameters isotherm; Koble-Carrigan isotherm and Langmuir-Freundlich isotherm ($R^2 = 0.9999$) fitted with the experimental results better than Redlich-Peterson model ($R^2 = 0.5$).

Keywords: nitrate; kinetic; isotherm; rice straw; adsorption; waste management.

1. INTRODUCTION

Highly contaminated water with nitrates leads to many serious problems which affect human health and environment [1]. Such as water eutrophication phenomenon which causes an extremely failure and damage in the water ecosystem because, excessive nitrate intake in water leads to an excessive growth in algae and aquatic plants [2]. Stomach cancer is a result of the high nitrate concentration in water. When nitrate is reduced to nitrite in the human body then it combined with haemoglobin, this leads to prevention of oxygen carrying to body cells and this phenomenon is called methemoglobinemia or blue baby syndrome [3]. The denitrification from aqueous solutions can be achieved by various methods; biological denitrification, ion exchange, chemical reduction and reverse osmosis process using semi-permeable membrane [4]. Biological treatment usually requires biomass waste disposal which is produced in sufficient amounts. Also, it usually requires pH control and an external organic carbon source in order to reduce nitrate to nitrogen gas [5], [6]. Ion exchange and reverse osmosis treatment processes remove many contaminants including nitrate also, their design is complex and lead to a second pollution which results in increasing of the overall process cost [7]. Supporting of iron nano particles can be achieved by several supporting materials in order to overcome the agglomeration problem of iron nano particles alone, increasing in their immobilization and catalytic efficiency. These supporting materials are such as activated carbon, biochar, nano-graphenes, clay materials and silicon. Rice is one of the abundant agricultural crops in the world. Million tonnes per year of rice are produced, causing production of significant quantities of rice straw wastes. Burning of rice straw leads to air pollution due to the high increase in the black cloud emissions [8]. In this

research the rice straw is used as a carbon support for the iron nano particles where rice straw is only acid activated then used as a support for nZVI particles. Production of such a modified rice straw adsorbent results in decreasing in the amount of produced rice straw waste which can increase the environmental remediation.

2. SYNTHESIS OF MRS ADSORBENT

Figure-1 presents the preparation scheme of the modified rice straw (MRS) adsorbent. Washing rice straw with distilled water for several times in order to remove attached heavy particles followed by drying for a day in the sun. Then, rice straw grinding to obtain it as a powder. Rice straw acid activation was carried out by using concentrated sulphuric acid (98%) in a ratio of (25gm : 25ml) at room temperature followed by washing for several times with distilled water till reaching neutral pH. Then, drying in an oven at 60 °C for 3 hrs [9]. The precipitation of iron nano particles on the surface of acid activated rice straw was achieved by mixing of 300 ml ethanol and water in a ratio of (20:80) (V/V), 0.1 M L-ascorbic acid and 200 mg of the acid activated rice straw powder in a three necked bottle for 40 min, followed by addition of 0.1 M $FeCl_3 \cdot 6H_2O$, stirring for another 40 minutes till all of the $FeCl_3 \cdot 6H_2O$ dissolved in the solution mixture. The insitu-reduction of iron nano particles on the surface of the acid activated rice straw was carried out by dropping of 300 ml of 0.16 M $NaBH_4$ dissolved in 0.1 M sodium hydroxide into the solution mixture at a rate of one drop per two seconds using a rotating speed of 150 rpm for 2 hrs at room temperature and under aerobic conditions [10]. Vacuum filtration of the produced adsorbent was achieved by washing for several times with ethanol (70%) followed by drying in a vacuum oven for 24 hrs at 40 °C and finally storing it in a vacuum desiccator.



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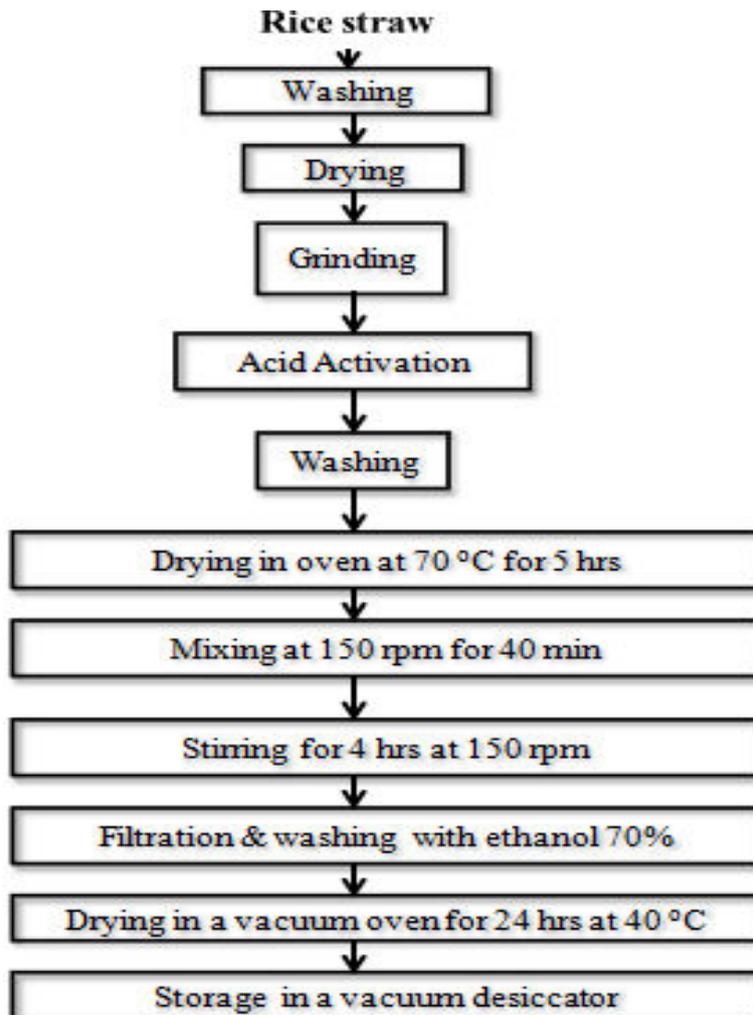


Figure-1. MRS adsorbent preparation scheme.

3. BATCH ADSORPTION EXPERIMENTS

Batch experiments were performed to determine the efficiency of the synthesized adsorbent in nitrate removing using four effecting factors including initial solution pH from 2, 7 and 12 which were adjusted by using 0.1 M NaOH and 0.1 M HCl solutions, initial nitrate concentration (6 mg/L, 23 mg/L and 40 mg/L), adsorbent dose (2 g/L, 2.5 g/L and 3 g/L) and contact time (5 min, 92.5 min and 180 min). Experiments were performed in

glass conical flasks and they were shaken vigorously at 150 rpm. Upon shaking, samples were separated by using a magnet, and then filtered. The concentration of nitrate in the filtered solution was measured by using a UV/VIS spectrophotometer.

4. RESULTS AND DISCUSSIONS

Table-1 represents the experimental values of nitrate removal.

**Table-1.** Experimental values of nitrate removal.

Run	pH	NO ₃ ion concentration	Adsorbent dose	Contact time	NO ₃ ion concentration after adsorption	Percent Nitrate Removal
		mg/L	g/L	min	mg/L	%
1	2	6	3	180	0.025	99.58
2	2	6	2	5	0.363	93.94
3	7	23	2.5	92.5	3.5	84.77
4	7	23	2.5	180	3.18	86.14
5	2	6	3	5	0.16	97.26
6	7	23	2	92.5	5.92	74.26
7	2	6	2	180	0.31	94.86
8	12	6	2	180	5.07	15.5292
9	2	40	3	180	6.44	83.9
10	12	23	2.5	92.5	19.63	14.64
11	12	40	2	5	38.63	3.4149
12	7	6	2.5	92.5	0.33	94.45
13	12	6	3	180	3.85	35.7456
14	2	23	2.5	92.5	2.21	90.4
15	7	23	2.5	5	5	78.27
16	2	40	3	5	7.64	80.89
17	7	40	2.5	92.5	15.72	60.68
18	12	6	2	5	5.17	13.7823
19	12	40	3	180	36	10.0802
20	2	40	2	180	10.71	73.22
21	12	40	2	180	38.34	4.126
22	2	40	2	5	11.7	70.77
23	7	23	3	92.5	1.7	92.68
24	12	6	3	5	4.15	30.7211
25	12	40	3	5	36.22	9.4555

5. ADSORPTION KINETICS

The adsorption kinetics of nitrate by MRS adsorbent was studied at the following conditions; initial pH = 7.4, initial nitrate concentration = 6 mg/L, temperature = 25 °C, contact time = 180 min and adsorbent dose = 2.5 g/L. The experimental data fitted to the kinetic models Pseudo first order and Pseudo second order which were described by the following equations:

$$\text{Pseudo first order: } \log(q_e - q) = \log(q_e) - \frac{k_1 \cdot t}{2.303} \quad (1)$$

$$\text{Pseudo second order: } \frac{t}{qt} = \frac{1}{k_2 \cdot q_e^2} + \left(\frac{1}{q_e}\right) \cdot t \quad (2)$$

The initial adsorption rate (mg/L.min) was described by the following equation:

$$h = k_2 \cdot q_e^2 \quad (3)$$

Where q_e and q_t are the amounts of nitrate adsorbed by adsorbent at equilibrium and at time (t), respectively. k_1 , k_2 are rate constants for Pseudo first order and Pseudo second order, respectively [11], [12], [13]. Figures 2 and 3 represented the kinetic model application on the experimental results.

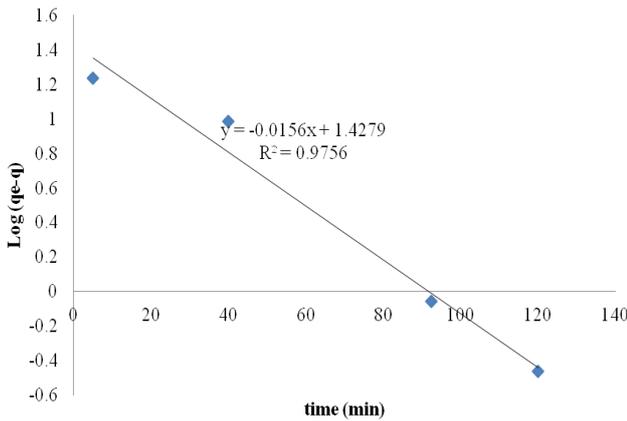


Figure-2. Pseudo first order kinetics model for nitrate removal by the MRS adsorbent.

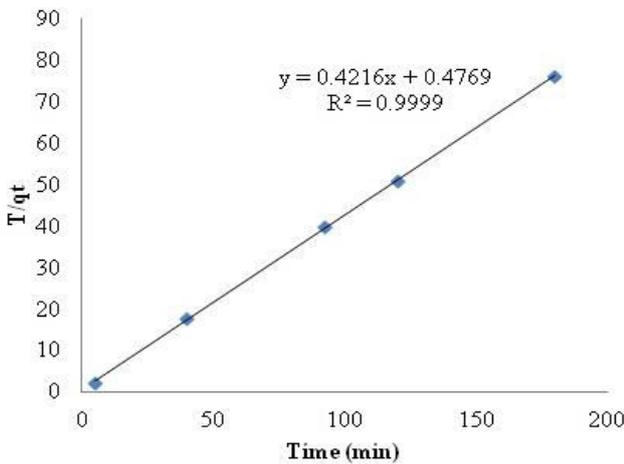


Figure-3. Pseudo second order kinetics model for nitrate removal by the MRS adsorbent.

Table-2 represented the parameters of kinetic models; the correlations coefficients (R^2), initial adsorption rate (h), k_1 and k_2 are rate constants for Pseudo first order and Pseudo second order kinetic models, respectively.

Table-2. Pseudo first order and Pseudo second order kinetic models parameters.

Kinetic model	Parameters	
Pseudo first order	q_e (exp) (mg/g)	2.36408
	q_e (calculated) (mg/g)	6.14469
	k_1 (min^{-1})	0.01612
	R^2	0.872
Pseudo second order	q_e (exp) (mg/g)	2.364
	q_e (calculated) (mg/g)	2.100
	k_2 (mg/g. min)	0.5381
	h (mg/L.min)	3.0078
	R^2	0.9999

The results in Table-2 concluded that the pseudo-first order model was not suitable for the nitrate adsorption by MRS as the calculated value of adsorption capacity at equilibrium (q_e) showed higher difference with the experimental value than the pseudo second order model. Also, the pseudo-first order model showed lower correlation coefficient value ($R^2 = 0.872$) for nitrate adsorption than the pseudo-second order model ($R^2 = 0.9999$). Therefore, the nitrate adsorption by MRS adsorbent could be well represented by the pseudo-second order kinetic model.

As the nitrate adsorption by MRS suggested model was the pseudo second order kinetic model which indicated that a chemisorption process occurred so, the rate limiting step for this system was determined by the intraparticle diffusion model and Byod plot. The intraparticle diffusion model could be represented by the following equation[14], [13]:

$$qt = k_{diffusion} * T^2 + C_i \tag{5}$$

Where qt is the amount of nitrate adsorbed at time (t) and C_i is the thickness of layer and $k_{diffusion}$ is the adsorption rate constant of intraparticle diffusion model.

The Byod plot was determined using the following equations[14]:

$$F = \frac{qt}{q_{max}} \tag{6}$$

Where the q_{max} is the maximum adsorbed amount of nitrate and F is the fraction of the adsorbed nitrate at any time (t).

The Bt values could be calculated at different contact times through the following equation[14]:

$$Bt = -0.4977 - \ln(1 - F) \tag{7}$$

Where B_t is the mathematical function of F .

Figure-4 represented the intraparticle diffusion model plot where the first linear portion represented the occurrence of film diffusion followed by another linear portion which represented the occurrence of intraparticle diffusion.

Byod plot is used to predict the actual limiting step involved in the adsorption process by plotting the B_t values vs. time (t) [14].

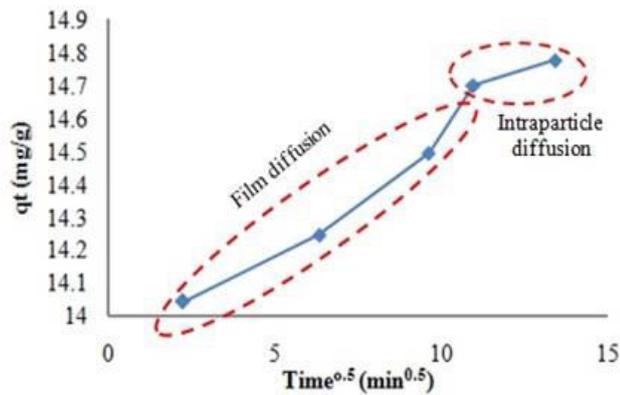


Figure-4. Intraparticle diffusion model for nitrate removal by MRS.

Byod plot suggested that the actual slowest step was the film diffusion as the plot was linear and didn't pass through the origin as represented in Figure-5.

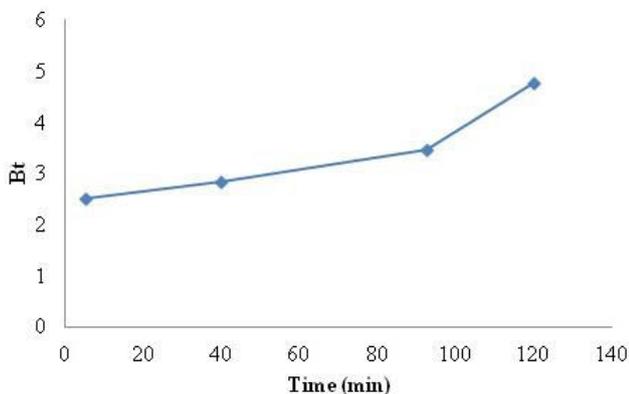


Figure-5. Byod Plot for nitrate removal by MRS.

6. ADSORPTION ISOTHERM STUDIES

Two and three parameters isotherm models were studied to fit the experimental data obtained from the effect of nitrate ions concentration (6 mg/L to 40 mg/L) on adsorption. Three parameters isotherm models are accurate than two parameters isotherm models because, they have three constants in their equations.

6.1 Two Parameters Isotherm Models

6.1.1 Langmuir isotherm

Langmuir isotherm model is concept of the monomolecular adsorption on homogeneous surfaces. Langmuir is represented by the following equation [12], [15], [16]:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) * C_e + \frac{1}{q_m * K_L} \quad (8)$$

Where C_e and q_e represent the concentrations of nitrate at equilibrium (mg/L) in solution and in solid phase, respectively. q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir

constant which indicates the adsorption energy (L/mg). The values of q_m and K_L can be determined from the linear plot of C_e/q_e versus C_e .

6.1.2 Freundlich isotherm

This model is used to give information of the adsorption characteristics for the heterogeneous surface. Freundlich isotherm is represented by the following equation:

$$\text{Log} q_e = \text{Log} K_F + \frac{1}{n} * \text{Log} C_e \quad (9)$$

Where K_F (L/mg) and n are the Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively [12], [16].

6.1.3 Halsey isotherm

Halsey isotherm is used for multilayer adsorption system and heterogeneous surfaces for adsorption of metal ions at a relatively large distance from the surface [16]. Halsey isotherm is represented by the following equation:

$$\text{Ln} q_e = \frac{1}{n_H} * \text{Ln} K_H - \frac{1}{n} * \ln \frac{1}{C_e} \quad (10)$$

Where K_H and n_H are the Halsey constants. Figure-6 represented the Halsey isotherm kinetic model.

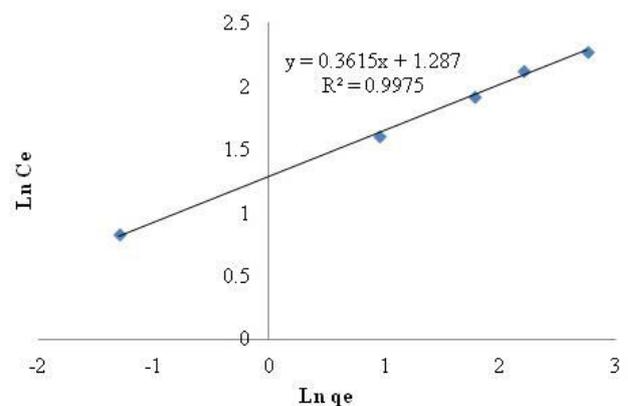


Figure-6. Halsey isotherm model for nitrate removal by MRS.

6.2 Three Parameters Isotherm Models

6.2.1 Langmuir-Freundlich isotherm

Langmuir-Freundlich isotherm characterizes the distribution of the adsorption energy onto the adsorbent's heterogeneous surface. Langmuir-Freundlich isotherm could be expressed by the following equation:

$$q_e = [q_m * (K_L * C_e)^n] / [1 + (K_L * C_e)^n] \quad (11)$$

Where q_m is maximum adsorption capacity (mg/g), K_L is equilibrium constant for heterogeneous adsorbent and n is heterogeneous parameter which lies in between 0 and 1. Nonlinear regression method can be used to determine these parameters [17].



6.2.2 Koble-Carrigan isotherm

The Koble-Carrigan isotherm model is a combination of Langmuir and Freundlich isotherms which is used to represent the equilibrium adsorption data. Koble-Carrigan isotherm is expressed by the following equation:

$$q_e = A.C_e^n / (1 + B.C_e^n) \quad (12)$$

Where A ($L^n.mg^{1-n}/g$), B (L/mg)ⁿ and n are the Koble-Carrigan constants, n is exponent that lies between 0 and 1 and q_e is the amount of pollutant which is adsorbed on the sorbent at equilibrium (mg/g) [16], [17], [12].

6.2.3 Redlich-Peterson isotherm

The Redlich-Peterson isotherm model is applicable for either heterogeneous or homogenous adsorption systems due to its characterization. Redlich-Peterson isotherm is expressed by the following equation:

$$q_e = A.C_e / (1 + B.C_e^\beta) \quad (13)$$

Where B is a constant (L/mg), A is the Redlich-Peterson isotherm constant (L/g), C_e is the equilibrium

concentration (mg/L), β is exponent that lies between 0 and 1 and q_e is the amount of pollutant which is adsorbed on the sorbent at equilibrium (mg/g) [16], [12], [17].

Table-3 represented the results of the two and three parameters isotherm models. The best fitted isotherm models were Freundlich and Halsey as they had the greatest correlation coefficient value ($R^2 = 0.997$) while Langmuir isotherm model has ($R^2 = 0.973$), respectively. In the Freundlich isotherm model the value of $1/n$ parameter (0.361) was less than 1 which indicated the suitability of the adsorption process for the Freundlich isotherm model. This result actually indicates the surface heterogeneity of the adsorbent and the adsorption process operated under multilayer adsorption. It was found that the Halsey isotherm model is an excellent model to describe the multi-layer behaviour of adsorption [16]. For three parameters isotherm models; Langmuir-Freundlich isotherm and Koble - Carrigan isotherm models were best fitted with the experimental results as they had the greatest correlation coefficient ($R^2 = 0.999$) than the Redlich-Peterson model ($R^2=0.5$). The value of parameter n in Koble-Carrigan isotherm model was 0.3828 which is closed zero, this indicated that the equilibrium isotherm model was approaching to Freundlich equation and the nitrate adsorption mechanism is heterogeneous [18].

Table-3. Results of the two and three parameters isotherm models for nitrate adsorption by modified ice straw.

Two parameters models	Freundlich	R^2	0.997
		$1/n$	0.361
		n	2.77
		K_F (L/mg)	3.614
	Halsey	R^2	0.997
		n_H	2.77
		K_H (L/mg)	3.5650
	Langmuir	R^2	0.973
		qm (mg/g)	10.869
K_L (L/mg)		0.41818	
Three parameters models	Langmuir - Freundlich	R^2	0.9999
		qm (mg/g)	101.22
		n	0.38916
		K_L	0.00021
	Koble - Carrigan	R^2	0.9999
		A	3.68166
		B	0.02623
		n	0.38283
	Redlich - Peterson	R^2	0.5
		A	10.9916
		B	73.3042
		β	-0.5542



7. CONCLUSIONS

Synthesis of the MRS adsorbent for nitrate removal was developed with lower energy consumption method than the energy valorization process. Also, the synthesis of this adsorbent contributed in removal of nitrate and rice straw waste which can increase the environmental remediation. Pseudo second order kinetic model was the best model to describe the nitrate adsorption by MRS adsorbent which indicated that a chemisorption process occurred. The rate limiting step was determined using intraparticle diffusion model and Byod plot which illustrated that film diffusion was the rate limiting step for this system. Freundlich and Halsey isotherms were the best fitted model to describe this adsorption system. The optimum nitrate removal 94.8 % was achieved at pH= 7, adsorbent dose 3 = g/L, 150 rpm, initial nitrate concentration = 23 mg/L and contact time 180 = min.

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