

Ammoniacal Nitrogen Removal Using flamboyant pods (*Delonix Regia*) Adsorbent for Natural Rubber Wastewater Treatment

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Abstract: Plant waste such as *Delonix Regia* Pods (DRP) have the potential to be used as adsorbents. A study of lignocellulose *delonix regia* pods was carried to assess ammoniacal nitrogen removal from natural rubber wastewater. Sample wastewater was taken from the rubber processing industry and characterization was carried out. Outcomes from the analysis shows that the ammoniacal nitrogen concentration was 66 mg/L and higher than the recommended wastewater discharge standards. Batch experiments were conducted on the effect of dose, pH, shaking speed and contact time parameters for optimum condition. The results revealed that the optimal dosage, pH, shaking speed and contact time is 4.5 g, pH 8, 150 rpm and 120 minutes with ammoniacal nitrogen removal efficiency of 74.3 % and the adsorption capacity of 1.22 mg/g. Pseudo second order kinetic model was found to fit the data better and the R^2 obtained was 0.9992. From the study, it can be concluded that the media can be used for the removal of ammoniacal nitrogen in natural rubber wastewater and subsequently reduce environmental pollution. Hence, it can be sustainable and environmentally friendly.

Keywords: Rubber wastewater, lignocellulose, adsorption, *delonix regia* pods

1. Introduction

Different treatment procedures have been published for the remediation of inorganic and organic contaminants such as biological method of treatment, physical and chemical treatment, advanced oxidation among others. The bulk of these methods of treatment are satisfactory, but limited due one or more reasons, for example in biological treatment (anaerobic digestion stabilization ponds, trickling filters, aerated lagoons) take place involving bacteria and microorganisms and these living organism are most effective under suitable conditions, which can vary with change in oxygen concentrations contained in the effluent. Advanced oxidation approach are economically expensive and can have problems of chlorine oxidation. Other types of treatments such as ozonation [1-3], coagulation–floculation [4] also have been used in investigations but have economic cost. Generally, many methods have been applied for the treatment of wastewater and adsorption remained the most preferred because of the ease in operation as well as its global application. The available

marketed adsorbents such as granular activated carbon have proven as efficient for the treatment wastewater, which is attributable to the high capacity in adsorption and porous structure. Nevertheless, commercially obtainable carbons are costly unsustainable, which necessitates research to develop low-cost adsorbents. Numerous works were undertaken to investigate the usage of industrial and agricultural waste product as low-cost adsorbents in favour of the treatment of wastewater. Among the low-cost adsorbents found in literature are; fly ash, peat, bone char, cockle shells, bagasse [5-8] and these have demonstrated efficient applicability as alternatives for remediation of contaminants from wastewater. Based on literature it was ascertained that *Delonix regia* pods activated carbon as an adsorbent is hardly been used for the remediation of ammonia from rubber industry wastewater.

Natural rubber is one of the key sectors of agro-based industries in the Southeast Asian region. More than 60% of natural rubber production worldwide comes from Thailand, Indonesia, and Malaysia [9]. The processing of natural rubber for its products requires large quantities of

water during its operation, the rapid industrial advancement in Malaysia has been accompanied by comparatively large effluent discharge. The effluent is composed of different types of contaminant as well as high concentration of ammonia nitrogen which if not treated can pose a serious threat to the environment [9-12]. Therefore, de-ammoniation of rubber wastewater employing sustainable methods is inevitable. This article explores the minimization of the ammonia content from rubber industry wastewater using a novel adsorbent made from Delonix Regia Pods activated carbon.

2. Wastewater Sampling

Rubber wastewater samples were collected from the effluent of the rubber industry plant located in Kluang, Johor using plastic polytetrafluoroethylene (TFE) bottles. Samples were taken to the laboratory as soon as possible and stored in a cold room at 4° C to prevent changes that may take place due to chemical and biological activities. All chemical and reagents for the characterization of rubber wastewater was conducted in accordance to the Standard Methods for the Examination of Water and Wastewater [13].

3. Media Preparation

Flamboyant (Delonix regia pods) were washed completely with distilled water so as to remove impurities and then oven dried at 105° C for 24 hours and cooled to room temperature. The Flamboyant was trimmed to 5-10cm and pulverized using grinder (Model fritz). Subsequently the grinded powder was sieved to obtain particle sizes 150mm. 10 grams of Flamboyant powder was weighed and mixed in 100 ml of distilled water with 0.5 M citric acid at room temperature. Then, the mixture was stirred for 60 minutes and washed with distilled water to clean the citric acid solution. The powder was again dried in an oven at 50° C for 24 hours and the temperature was subsequently raised to 90° C for 90 minutes and then cooled [14].

4. Wastewater Experimental Sampling

All experiments were conducted using 100ml of rubber wastewater in a 250 ml Erlenmeyer flask reactor mixed with the adsorbent. The batch study was carried out by varying dosage, pH, shaking speed and contact time using laboratory orbital shaker. After a predetermined time the flask was then removed and allowed to settle. The pH adjustment was done using NaOH and H₂SO₄. And the supernatant was withdrawn for analysis of ammoniacal nitrogen.

The percentage removal was calculated according to equation (1);

$$\% \text{ Removal} = (C_i - C_f) / C_i \quad (1)$$

Where C_i and C_f represent initial and final concentration respectively [15].

5. Results and Discussion

5.1 Wastewater characterization

Table 1, shows the characteristics of the rubber wastewater obtained from the rubber industry. These values are high when compared to Department of Environment Malaysia; Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and standard B [12]. The ammonia nitrogen is significantly above the requirements of the standard. And also it is essential to reduce the concentration according to the standard before being discharged to any water body.

Table 1: Rubber wastewater characteristics.

Characteristics	Unit	Value
Biological Oxygen Demand (BOD)	mg/L	3345
Chemical Oxygen Demand (COD)	mg/L	5215
Total Suspended Solids	mg/L	506
Ammoniacal Nitrogen (NH ₃ -N)	mg/L	66
Color	Pt.Co	349
Turbidity	NTU	130
Zinc	mg/L	0.261
Iron	mg/L	0.08
Cu	mg/L	0.035
pH		9.2

5.2 characterization of media

The results obtained from the characterization of the chemical composition of the media are presented in Table 2. Evidently the carbon content is relatively high, which indicates its potential for a favorable adsorption process.

Table 2: Percentage of the chemical composition of adsorbent.

Media	%
O	22.09
Si	0.26
Al	0.11
K	0.09
C	56.13
N	21.27

5.3 Batch studies

5.3.1 Effect of adsorbent dosage on ammoniacal nitrogen removal

A series of experiments were conducted by varying the adsorbent doses from 0.5 to 6 g and mixed with 100mL of rubber industry wastewater and agitated using an orbital shaker at 150 rpm and 120 minutes contact time. The flask were then withdrawn and allowed to settle. The supernatant was then withdrawn and analyzed.

Figure 1 shows the effect of adsorbent dosage on the percentage of ammoniacal nitrogen removal and adsorption capacity for delonix regia pods. The highest percentage removal occurred at dosage of 4.5 g with 70.9 % removal efficiency and an adsorption capacity of 1.10 mg/g. Initially, there was a gradual increasing trend in

removal up to 4.5g dosage, thereafter it remained constant.

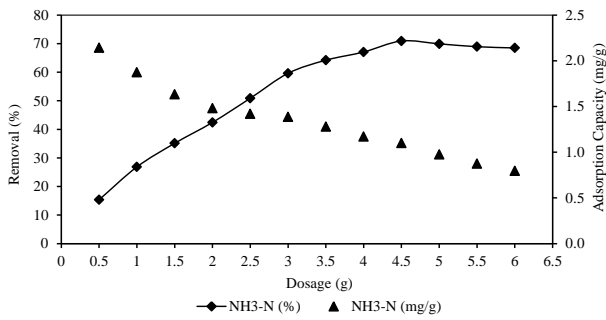


Figure 1: Effect of adsorbent dosage on ammonia removal.

This may have taken place because when the adsorbent was added, there was more available adsorption sites and a corresponding increase in removal occurs. At 4.5g dose the adsorbent may have reached equilibrium such that additional dose can have no effect on removal and other factors such as agitation may have also caused the particles to impact on each other due to kinetic energy creating an adsorption – desorption cycle at the equilibrium state [16].

5.3.2 Effect of pH on ammoniacal nitrogen removal

A series of experiments were conducted by varying the pH of the wastewater from pH 3 to 12 and the adsorbent mixed with 100mL of the water and a dosage 4.5 g, agitated at 150 rpm for 120 minutes contact time. Figure 2 shows the effect of pH on the efficiency and adsorption capacity of the media. The highest percentage removal occurred at pH 8 with a corresponding efficiency of 73.7 % and an adsorption capacity of 1.08 mg/g. As seen from the figure there was a gradual increase in removal efficiency with increase in pH up to pH8, thereafter any increase in pH did not increase the removal. This phenomena may be because, as the pH was increased the electrostatic interaction between the adsorbent and adsorbate is increased resulting in the increased removal efficiency due to the attraction forces. Above pH8 the surface charges decreases, and the efficiency also reduced due to electrostatic repulsion [17].

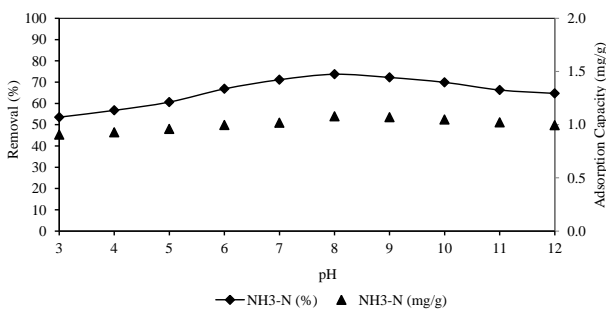


Figure 2: Effect of pH on ammonia removal.

5.3.3 Effect of shaking speed on ammonia removal

The effect of shaking speed was conducted by varying the shaking speed with increment rate of 25 from 50 to 175 rpm with 100mL of wastewater containing 4.5 g media dose, at pH8 and 120 minutes duration contact time. Figure 3 shows the effect of shaking speed on the ammoniacal nitrogen removal by the media. Based on the figure, the removal rate increased gradually from the lowest 50rpm to the maximum at 150rpm agitation which corresponded to the maximum efficiency of 74.9% and an adsorption capacity of 1.10 mg/g. Then the removal diminished with further increase in shaking speed. This may be because, as the speed was increased the kinetic energy of the adsorbate also was increased thereby increasing the diffusion of adsorbate through adsorbent boundary layer up to the maximum which signify the equilibrium state. However as the shaking speed increased above 150rpm, the efficiency was decreased, this may be because the increased speed caused the breaking of freshly formed bonds between the adsorbate and adsorbent media [18].

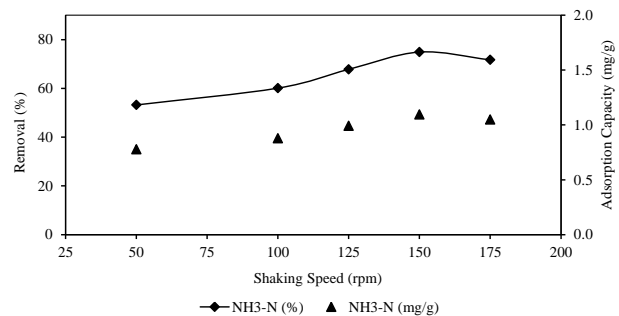


Figure 3: Effect of shaking speed on ammonia removal.

5.3.4 Effect of contact time on ammonia removal

A series of experiments were carried by varying the contact time between 5 to 160 minutes and using mixture of 4.5g adsorbent dose with 100mL of wastewater, the pH adjusted to 8 and shaking speed set to 150 rpm. Figure 4 depicts the effect of contact time on the percentage removal and adsorption capacity of ammonia nitrogen removal using the adsorbent media. It is evident from the graph that the removal had increased rapidly from the start up to the optimal removal at 120 minutes shaking time with adsorption efficiency of 74.3 % and the adsorption capacity of 1.22 mg/g. After 120 minutes time the removal did not increase with time. This probably is caused by saturation of the adsorbent with the adsorbate. Thereafter desorption due to saturation takes place and then re-adsorption process follows [19].

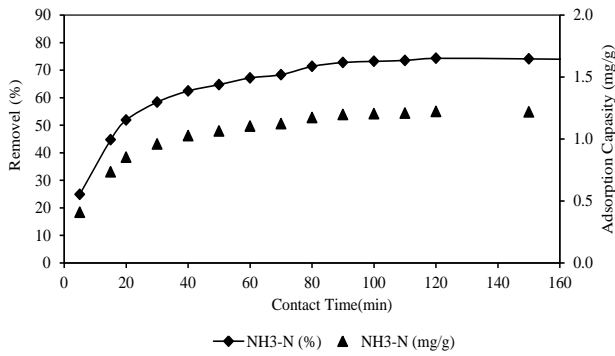


Figure 4: Effect of contact time on ammoniacal nitrogen removal.

6. Adsorption Kinetics

The adsorption kinetics model was used to analyze the mechanism and adsorption rate of ammoniacal nitrogen to media. The kinetic models used in this study is a pseudo first order and pseudo second order.

The assayed removal values against the adsorbent dose were regressed against the pseudo-first-order and the pseudo-second-order kinetic equations. The pseudo-first-order model is based on the assumption that the solubility rate with time is directly proportional to the saturation concentration and the absorbed amount, while the pseudo-second order adsorption mechanism is by chemisorption [20-22]. The first pseudo-first kinetic equation is represented by equation (2) and the pseudo-second-order by equation (3).

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t is the amounts of ammoniacal nitrogen adsorbed at time t and q_e is the uptake of ammonia per unit weight of adsorbent at equilibrium (mg/g). K_1 and K_2 are the adsorption rate constant for the pseudo-first order and second-order models respectively. The calculated (cal) values of q_e for the pseudo-first order was lower than the calculated (Table 3).

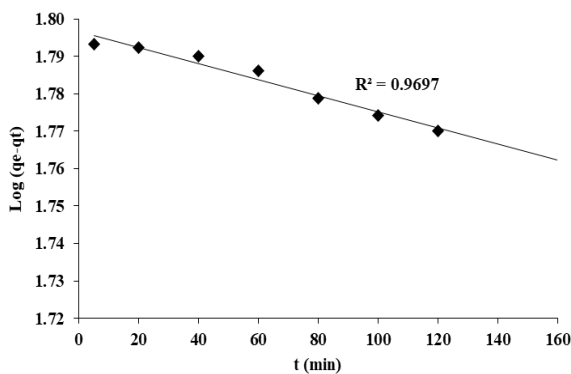


Figure 5: Pseudo first order model for the removal of ammonia using media.

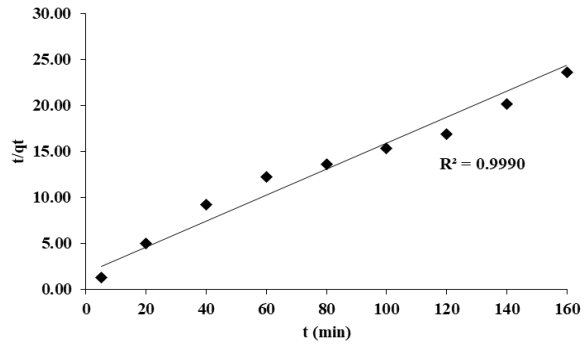


Figure 6: Pseudo second order model for the removal of ammonia using media.

However, based on the coefficient of determination R^2 (figure 5 and 6) the pseudo-second order was best fitted to the data than pseudo-second order. Therefore, the dominant adsorption mechanism can be described to be chemisorption. The result is also consistent with that in literature which reported that the reaction kinetics of similar media followed the psudo-second order model [23,24, 25, 26, 27]. The pseudo-first order and pseudo-second order rate constants (K_1 and K_2) were 0.0397 and 0.1300 respectively.

Table 3: Kinetic models parameter for ammoniacal nitrogen adsorption onto media.

Parameter	Ammoniacal Nitrogen
Experiment (Exp)	$q_e, \text{exp (mg/g)}$ 1.22
Pseudo-First-Order	$K_1 \text{ (1/min)}$ 0.0397
	$q_e, \text{cal (mg/g)}$ 1.05
	R^2 0.9697
Pseudo-Second-Order	$K_2 \text{ (g/(mg.min))}$ 0.1300
	$q_e, \text{cal (mg/g)}$ 1.37
	R^2 0.9990

7. Summary

Results of the study revealed that delonix regia pods performance in treatment was influenced by the pH, shaking speed, dosage and contact time parameter for the removal of ammoniacal nitrogen from the natural rubber wastewater. The optimal percentage removal of ammoniacal nitrogen achieved was 74.3% while the adsorption capacity was 1.22 mg/g. Based on the R^2 value (0.9990) the sorption process conforms to pseudo-second order reaction kinetic. Further research is recommended to determine the effectiveness of the media for the removal of other contaminants contained in rubber wastewater.

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