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# Experimental Approach for Chemical Oxygen Demand and Ammonia Nitrogen Removal from Natural Rubber Wastewater via Adsorption by Kaolin

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**Abstract.** Natural rubber is an important material because of its high strength compared to synthetic rubber. However, the production process of natural rubber discharges a large amount of wastewater containing high concentrations of organic compounds and nitrogen. Therefore, discharging natural rubber processing wastewater without an appropriate treatment can lead to environmental problems such as deterioration of water quality and eutrophication. In this study, the batch adsorption experiment was carried out for the removal of chemical oxygen demand (COD) and ammonia nitrogen from natural rubber wastewater using kaolin as adsorbent. The efficiency of the kaolin was studied by varying the parameters adsorbent dose, pH, shaking speed and contact time. The experimental equilibrium data for this system has been analyzed using the linearized forms of Langmuir and Freundlich isotherms. COD and ammonia nitrogen removal efficiencies were 71.6% and 75.8%, respectively. While, Langmuir isotherm was found to provide the best theoretical correlation of the experimental data.

## 1. Introduction

The rubber industries one of the main agricultural-based industry in area of South East region. Over 60% of world's rubber production arrives from Indonesia, Malaysia and Thailand [1]. Nevertheless,



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rubber manufacturing industries produces substantial amounts of waste water contain higher organic contents, ammonia and suspended solid [2]. The wastewater are derived during the process washing, cleaning and dilution [3].

An averagely, about 18-35 m<sup>3</sup> rubber industry wastewater contain higher concentration of organics content and ammonical nitrogen are released during manufacturing of 1ton of natural rubber products [1]. Without adequate treatment, the discharge of this wastewater into the environment may have serious, dangerous, and prolonged consequences [4].

Various biological treatment methods are being specifically formulated for raw effluent like anaerobic cum facultative lagoon, anaerobic cum aerated lagoon, aerated lagoon, and oxidation ditches [5]. Nonetheless, these methods have certain drawbacks, like huge area required, hydraulic residence time (HRT), electricity consumptions for aeration, discharge large amount of excessive sludge, harmful gases (malodorous emission), huge amount of greenhouse gas (GHG) emission, i-e., CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O [1]. Adsorption techniques widely known and commonly used approach for the treatment of organic and inorganic hazardous waste [6]. Adsorption study for waste water treatment was shown less costly and effective in treating waste water based on types of adsorbent used [6].

Adsorption on activated carbon (AC) or activated carbon adsorption is widely known technique for removal of hazardous wastes, due to its higher in cost the utilization of AC is restricted in developing countries [7], [8]. Nonetheless, because of its expensive cost and complexity in regeneration, lower cost, relatively more effective adsorbent clay, kaolin, zeolite, and bentonite are consider as low cost alternative adsorbent [9].

Clay mineral have several uses in many sectors of industry because of their large surface areas, thermal stability, porosity, active site and attracted adsorption property [8]. Kaolin have promises of recognize as adsorbent. Due to the higher adsorption ability, lower cost, abundant many continent worldwide and capability for ions exchange [8], [10]. Kaolin clays, which is made up of metals oxide such as Aluminium oxide, Silicon dioxide, Magnesium oxide and Calcium oxide is a worldwide abundant and naturally available minerals [11].

In the present research work, experiment were conducted utilizing kaolin adsorbent for removing of ammoniacal nitrogen and COD by adsorption techniques. Effects were investigated for adsorbent dosage, shaken speed and shaken time. The equilibrium data evaluated using isotherm model Langmuir and Freundlich.

## **2. Materials and Method**

### *2.1. Preparation of kaolin*

The kaolin adsorbent utilizing for this present analysis was collected from Tapah, Perak, Sdn Bhd, Malaysia. Kaolin were grinded and sieve to a scale of between 106-150 µm. The sample were then oven drying at 105°C for 1hour to eliminate excessive moisture, after that placed in desiccates (avoid ambient moisture) while it was checked. The characterization of kaolin clays material was used to determine by using spectroscopy (X-ray fluorescence, XRF).

### *2.2. Wastewater sampling*

The samples of rubber waste water manually collected from rubber industry located I district Kluang. The collected samples were stored in a cold house to prevent chemical variations in the waste water characterization, since samples change from day-to-day. The characteristics of this wastewater were

analyzed according to the standard methods for examination of water and wastewaters [12]. All chemicals used were of analytical grade.

### 2.3. Adsorption studies

Batch experiment were carried out to determine the process ranges that includes dose, shaken speed, shaken time and pH. Each variable were investigated and separately monitored. Experiment conducted in 250 mL volumetric glass using kaolin as a medium and 100 mL sample of rubber waste water. The glass cap was lined by laboratory thin film (Para-film M, USA), Ensuring sufficient agitation system. The packed glass was agitate with an orbital shaker (Sartorius, Germany). The glass were then remove and allowing to settled little before adding the supernatants for examine the COD and ammonia nitrogen [13].

### 2.4. Adsorption isotherms

Adsorption isotherm, explain how adsorbate reacts with adsorbent and clearly understand the nature of interacting. Isotherms help to provides detail about optimal adsorbent consumptions. So significantly improve the configuration of an adsorption method to remove COD and ammoniacal nitrogen from waste water, it is essential to establish the most appropriate correlation for the equilibrium curve [14]. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. However, the most common types of is otherms are the Langmuir and Freundlich models which used in this study.

## 3. Result and Discussion

### 3.1. Characteristics of adsorbent

Kaolin composition was studied using X-ray Fluorescence (XRF) as illustrated in table 1. Aluminium and silica are the predominant kaolin species, 31.6% and 49.9% respectively. The parent clay contains alumina and silica which are in major quantities where as other oxides such as magnesium oxide, calcium oxide, potassium oxide, zinc oxide and titanium oxide are present in trace amounts [15].

**Table 1.** XRF analysis data of kaolin.

Composition	Percentage
SiO <sub>2</sub>	64.5 %
Al <sub>2</sub> O <sub>3</sub>	15 %
Fe <sub>2</sub> O <sub>3</sub>	0.94 %
TiO <sub>2</sub>	0.16 %
CaO	3.23 %
MgO	0.70 %
Na <sub>2</sub> O	0.80 %
K <sub>2</sub> O	3.55 %
C	1.00 %
SrO	0.12 %

### 3.2. Wastewater characteristics

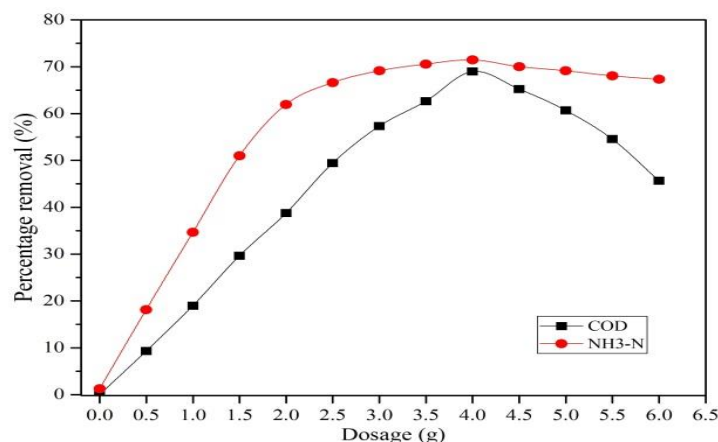
Table 2, indicates that this analysis is being used for waste water quality utilized in this research study. The waste water characterization are clearly shown in the table 2, such as COD value 5145 mg/L, ammoniacal nitrogen value 55 mg/L, suspended solid value 500 mg/L, BOD5 value 3350 mg/L, color value 345Pt.Co, turbidity value 87-172NTU and pH8.3-10.6. The characterized values were compared with the Department of Environment Malaysia; Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and B [16]. Thus, the value of heavy metals below permitted level.

**Table 2.** Characteristics of natural rubber industry wastewater.

Characteristics	Value
Biological Oxygen Demand (mg/L)	3350
Chemical Oxygen Demand ((mg/L)	5145
Total Suspended Solids (mg/L)	500
Ammonia Nitrogen (mg/L)	55
Colour (Pt.Co)	345
Turbidity (NTU)	130
Zinc (mg/L)	0.266
Iron (mg/L)	0.08
Cu (mg/L)	0.05
pH	9.3

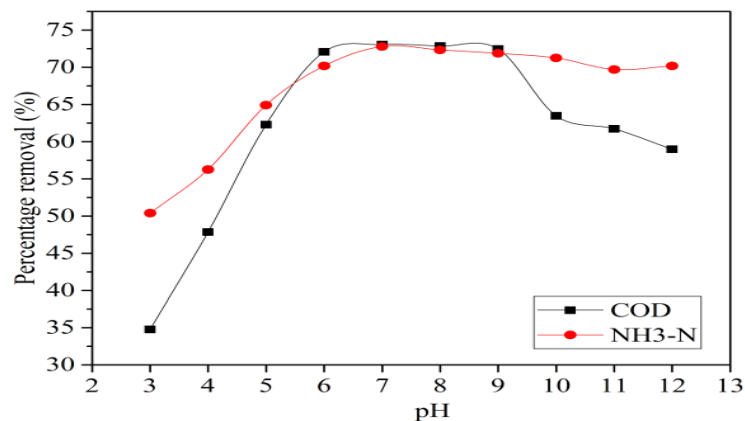
### 3.3. Adsorption studies

**3.3.1. Effect of dosage.** The availability and accessibility of adsorption site is controlled by adsorbent dosage [17]. Kaolin dosage was varied from 0 - 6 g as shown in the figure 1. The removal of COD and ammonia nitrogen efficiency increase with the increase of the AC dosage from 0 - 4 g. Then, the percentage removal begins to decrease with a further increment of the adsorbent dose. This behavior can be explained considering that when the amount of adsorbent increases, the amount of available adsorption sites increases until the optimum mass is reached; any further increase in the adsorbent dose may result in aggregation, which can decrease the probability of molecules contacting all available adsorption sites [18]. The best result obtained was 4 g of kaolin dosage with 69 % and 71.5% for COD and ammonia nitrogen removal efficiency respectively.



**Figure 1.** Effect of kaolin dosage on the adsorption % of COD and ammonia nitrogen.

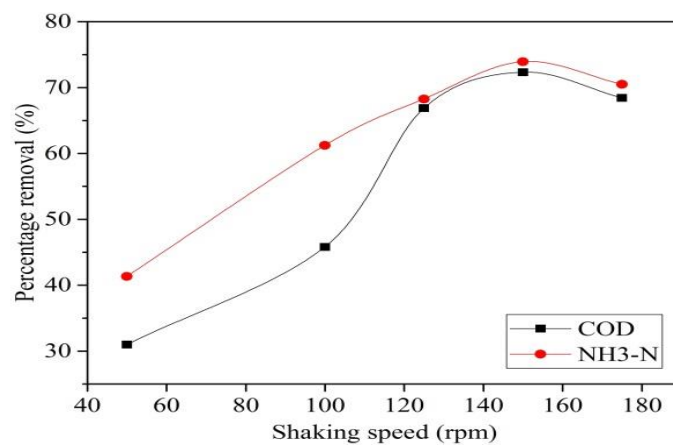
*3.3.2. Effect of pH.* The pH solution plays a vital role in process of adsorption because pH will affect polyprotic structure of adsorbate and amphoteric property of adsorbent surface. The experiment on adsorption were performed with variation of pH 3-12 as shown in the figure 2. Removal of COD and ammonia nitrogen increasing with increases value pH8, then the rate of increase was drop down gradually to pH10. This can be directly related to the kaolin surface which contains a huge active surface site [11].



**Figure 2.** Effect of pH on the adsorption % of COD and ammonia nitrogen.

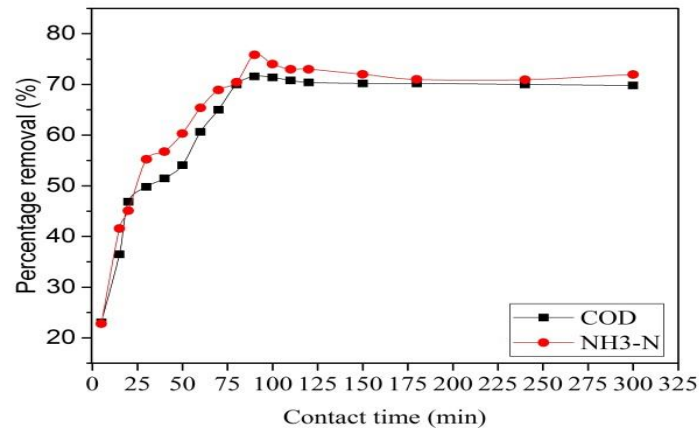
*3.3.3. Effect of shaking speed.* Figure 3 indicates removal percentage of COD and ammoniacal nitrogen at varying shaken speed 50, 100, 150, 125, and 175 rpm respectively. The shaken speed significantly effect on COD and ammoniacal nitrogen adsorption. For both adsorption decreased significantly at shaken speeds above 150 rpm. However, shaken speed of 150rpm indicates the most appropriate for this analysis.

Figure 3 illustrated that shaken speed leading to increased removal percentage of COD and ammoniacal nitrogen. This was because the rise in the agitation speed increased the diffusion particle to the adsorbent surface, and decreases in boundary layers around adsorbents [17].



**Figure 3.** Effect of shaking speed on the adsorption % of COD and ammoniacal nitrogen.

*3.3.4. Effect of contact time.* The relationship between shaken time and percentage removal COD and ammoniacal nitrogen from natural rubber wastewater using kaolin clay is shown figure 4, 23.1% and 22.8% COD and ammonia nitrogen were removed within first 5 minutes of reaction, 49.8% and 55.2% at 30 min and 71.6% and 75.8% in 100 min COD and ammonia was removed respectively.



**Figure 4.** Effect of contact time on the adsorption % of COD and ammonia nitrogen.

The rapid rate of removal of pollutants, particularly the reaction time is within 5 minutes because more opened sites available for adsorption, on kaolin beginning of the reactions such sites are taken in by adsorption as reaction progresses, with an improvement in shaken time, before equilibrium was reached [19]. The slow uptake in the later stages is probably due to an attachment controlled process caused by less available active sites for sorption, while the slight decrease in percentage removal with further increase in contact time at 100 min may be due to the saturation of the surface of kaolin with wastewater ions followed by the subsequent adsorption and desorption processes [20].

### 3.4. Adsorption isotherms

The equilibrium adsorption isotherms of importance in the design of adsorption systems. Several adsorption isotherm equations are available and the Langmuir and Freundlich isotherms are selected in this study.

*3.4.1. Langmuir model.* Langmuir analyses form of a monolayer adsorbate onto the surface of adsorbent [8], [18]. The Langmuir equation (Langmuir, 1918) may be written as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (1)$$

Another characteristics parameters of Langmuir is the dimensionless factor (RL), called separation factor (RL): as presented in equation (2)

$$RL = 1/(1+bC_0) \quad (2)$$

Table 3 shows adsorption of COD and ammonia nitrogen onto kaolin is favourable.

**Table. 3** Parameters of isotherm for removal of COD and ammonia nitrogen onto kaolin.

Isotherm model	COD	Ammonia nitrogen
Langmuir		
qm (mg/g)	222.22	2.9351
B (L/mg)	0.0007	0.0772
RL	0.21	0.19
R <sup>2</sup>	0.9993	0.9988
Freundlich		
KF	0.5673	0.2234
n	1.3378	1.2976
R <sup>2</sup>	0.9918	0.9924

3.4.2. *Freundlich model.* Freundlich is an experimental techniques which described heterogeneous adsorption surface wherein the adsorbate concentration is increased with rise in the initial solution concentration [18]. The Freundlich equation was represented as

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$

KF, and n, respectively, shows adsorption capability and strength. KF seems to be an essential constant for the adsorption efficiency as a useful term. The (1/n) slope varying from 0 to 1 is measuring adsorption strength or heterogeneity of the surface and becomes more heterogeneous although the values approached zero [8]. The reading of 1/n less than one indicate normal Langmuir, whereas, 1/n greater than one indicate co-operative adsorption.

Table 3 illustrated value of n for kaolin are 1.34 and 1.30, respectively, indicating that the parameter COD and ammonia nitrogen are favourably physically adsorbed onto kaolin. The correlation factors for two studied isothermic model were tested and compare to determine the best suited model. The Langmuir and Freundlich parameter for ammoniacal nitrogen and COD adsorption with fresh and cold-plasma treated with kaolin samples as described table 3. The Langmuir correlation higher than Freundlich obtained value. Consequently, Langmuir are observed to better match equilibrium data for ammoniacal nitrogen and COD adsorption on kaolin.

#### 4. Conclusion

For this research analysis, adsorption performance through kaolin as cost effective adsorbent were investigated for the removal of ammoniacal nitrogen. Experiment result revealed that, the optimal condition for adsorption were identified to be 4g of dosage, pH7, 150rpm shaken speed and 90minutes of shaken time. Freundlich and Langmuir isotherm studies exhibited that kaolin favourable batch adsorption for removing ammoniacal nitrogen and COD from natural rubber wastewater. In order to determine the coefficient of ammoniacal nitrogen and COD, adsorption was best suited to Langmuir. The finding result shows kaolin potentially effective as such an alternative cost effective adsorbent in rubber

waste water treatment. However, further performance may be obtained by improving kaolin media used acid based treatment and or surfactant impregnation.

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