Journal of Renewable Energy, Electrical, and Computer Engineering
Volume 4, Number 1, March 2024. 42-47
eISSN 2776-0049
DOI: https://doi.org/10.29103/jreece.v4i1.14673
Research Original Article

Utilization of Molasses Waste as Activated Carbon for Adsorption of Rhodamine B from Synthetic Waste

Ali Nur Muhammad Zaidin Balatif, **Muhammad***, **Rizka Mulyawan**
Chemical Engineering, Universitas Malikussaleh, Kampus Utama Cot Teungku Nie Releut, Muara Batu, Aceh Utara
*Corresponding Author: mhdtk@unimal.ac.id | Phone: +6282163307616

Received: January 04, 2024 **Revision: February 18, 2024** **Accepted: March 20, 2024**

Abstract

The utilization of molasses waste as Rhodamine B adsorbent has been investigated by studying adsorption isotherm and adsorption kinetics. The sample used is a variation of the concentration of Rhodamine B 10, 25, and 50 mg/L for kinetics adsorption and 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, and 250 mg/L for isotherm adsorption. Kinetic analysis adsorption being tested by pseudo-first-order and pseudo-second-order rate equation, as for the equilibrium equation being tested by Langmuir and Freundlich adsorption isotherms. Study shows that Langmuir equation model and pseudo-second-order are the most suitable to be applied. The adsorption constant is obtained of 1.1664 L/g and q_{max} of 221.8279 mg/g in Langmuir Equation. Whereas for pseudo second order equations obtained values of qe, $_{exp}$ and qe, $_{cal}$ which are slightly different. The qe, $_{cal}$ values obtained were 8.142 mg/g, 23.141 mg/g, and 53.895 mg/g for various concentrations. K value is obtained with a range of 0.001754-0.000294 and a value of R^2 with a range of 0.8249-0.995 for various concentration. Intraparticle diffusion in this study is not the only rate control measure due to the plot linear at each concentration does not cross the origin

Keywords: Adsorption; Molasses; Rhodamine B

Introduction

Pollution due to industrial and human activities is a very serious concern these days. Textile and paper industry effluents are one of the major contributors to water pollution. Rhodamine B ($C_{28}H_{31}ClN_2O_3$) is one of the dyes in the textile industry. Rhodamine B is a synthetic dye in the form of crystalline powder, odourless, green or reddish purple in colour and commonly used to dye cotton, wool, straw, silk, and bamboo. Rhodamine B is a compound that is difficult to degraded naturally by microorganisms because it has a structure consisting a base amino group and a benzene core. Rhodamine b is a toxic compound because it contains alkylating that if contaminated in the human body can cause dermatitis, slimy skin, diarrhea, kidney damage, anemia, cancer, and liver failure (Mahatmanti et al., 2017).

Molasses is one of the wastes produced by sugar factories in the form of viscous liquid that has a brown colour obtained from the crystallization of sugar. Molasses can no longer be formed into sugar but still contains sugar content with a concetration around 50.23% (Wardani & Pertiwi, 2013). Molasses is a very common product and an economical carbon source sompared to other sugar sources (Joshi et al., 2008). Adsorption of dye waste generally uses activated carbon and chitosan as adsorbents. Chitosan as a adsorbent has been widely used but has a disadvantage that chitosan is easily soluble at low pH so it is not able to adsorb adsorbate at low pH conditions because the active site (amine group) of chitosan is protonated and its adsorption ability is easily influenced by anion in the water (Joshi et al., 2008). Activated carbon is an amphoteric that can be negatively and positively charged and depends on the pH pf the solution tu adsorb organic and inorganic materials. Activated carbon (Siregar et al., 2021) as a dye adsorbent is one of the alternatives in dye waste treatment because it is more selective, competitive approach, effective, and cheap.

Materials & Methods

Materials

The Materials needed in this study are Molasses, Rhodamine B, H_2SO_4 96%, NaOH 4N, and aquadest.

Methods

The effect of pH was first studied. The initial pH of the solution was adjusted using either HCl or NaOH to obtain the desired initial pH at the range 2.0 to 11.0 that the pH readings were measured with a pH meter. Initial concentration of the solution and the adsorbent mass were fixed at 50 mg/L and 0,3 g, respectively. The studies were carried out at 30°C to investigate the optimum initial pH that will give the higest percent removal of the adsorbent after 2 hour.

Batch sorption studies were performed at different Rhodamine B concentrations 50, 100, 150, 200, and 250 mg/L to obtain the equilibrium isotherms and 10, 25, and 50 mg/L to obtain the kinetics adsorption with 0,3 g of mass adsorbent. Series of Erlenmeyer flask filled with 250 ml of Rhodamine B solution of varying concentrations and shaken using a shaker, which was operated at 150 rpm until reached equilibrium for isotherm studies and for 2 hour for kinetics studies. The samples were collected every 12 hours for isotherm studies and every 10 minutes kinetics studies. The samples solution that was free from adsorbent was analysed using Uv/Vis spectrophotometer at 553 nm wavelength.

The amount of Rhodamine B adsorbed per gram of carbon at given time, qt (mg/g), can be calculated from:

$$qt= \frac{V\ x\ (Co\text{-}Ct)}{m} \tag{1}$$

where C0 (mg/L) is the initial of Rhodamine B concentration in liquid phase, Ct (mg/L) is Rhodamine B concentration in liquid phase at given time, V (L) is total volume of Rhodamine B solution and m (g) is mass of adsorbent

Results and Discussion

Effect of Initial pH

One of the major parameters controlling the adsorption of Rhodamine B on sorbents is the value of pH. A change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites (Muhammad et al., 2011), (Hardi et al., 2022). The effect of initial pH on the adsorption equilibrium was studied by varying the initial pH of the solution with initial concentrations of 50 mg/L.

Figure.1 indicates the the effect of initial pH on the removal of Rhodamine B solutions onto activated carbon. It can be seen that the percent removal was very low at strong base condition. The percent removal decreased from 97,59% to 60,57% at initial pH 2,0 – 4,0, respectively. The maximum percent removal was observed at initial pH 2,0 for 97,59%. At low pH, Rhodamine B is present as a monomer, whereas at low pH higher the attractive electrostatic interactions between the carboxyl and xanthene groups of Rhodamine B monomer can increase the aggregation of dye molecules to larger dimers. Smaller monomer dye molecules can diffuses into the adsorbent micropores more easily than the dimer forms supports adsorption in an acidic environment (Wierzbicka et al., 2022). It is a common observation that the surface adsorbs anions well at low pH due to the presence of H^+ ions, whereas surface active for adsorption of cations at higher pH due to OH ion deposition (Jumasiah et al., 2005).

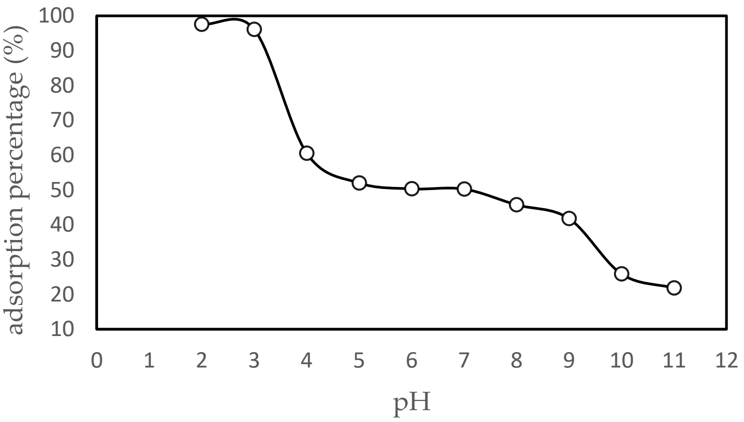


Figure 1. Effect of Initial pH

Isotherms Adsorption

Langmuir equation is the most widely used isotherm equation for modelling equilibrium which is valid for monolayer sorption onto surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface and is given by:

$$\frac{c_e}{q_e} = \frac{1}{K_L\ qm} + \frac{1}{qm}\ c_e \tag{2}$$

Where KL indicates the constant Langmuir adsorption (L/mg), Ce is concentration of adsorbate (mg/L), qe is amount of adsorbate adsorbed at equilibrium (mg/g), and qm is adsorption maximum capacity (mg/g). With the condition that Ce is the equilibrium concentration of the analyte in solution (mg/L). qe is the amount of analyte adsorbed at equilibrium (mg/g). KL is the Langmuir adsorption constant (L/mg). qm is capacity maximum adsorption (mg/g). The values of KL and qm can be determined by graphical relationships between Ce and Ce/qe (Hu et al., 2011).

The Freundlich isotherm describes equilibrium on a heterogeneous surface where energy of the adsorption is not equivalent for all adsorption sites, thus allowing multi-layer adsorption. The Freundlich equation is given as:

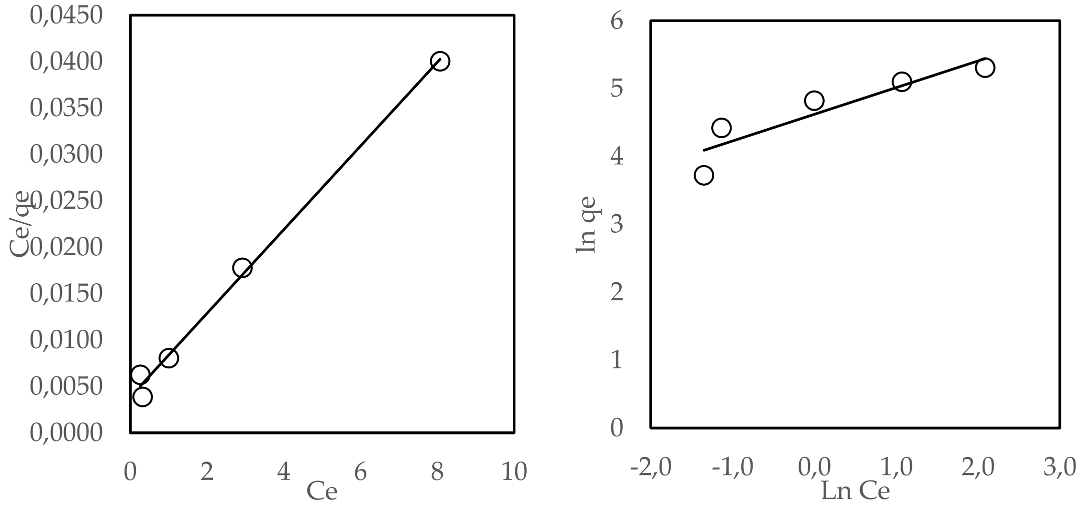
$$\ln q_e = \ln kf + \frac{1}{n} \ln C_e \tag{3}$$

where kf is the Freundlich constant (L/mg) and n is the Freundlich $_{exp}$onent. The plot of ln qe versus ln Ce produces a straight line with slope = 1/n and intercept = ln b.

Table 1. Isotherm Parameter on Rhodamine B Adsorption Using MAC

Parameter	Isotherm	
	Langmuir	Freundlich
qmaks (mg/g)	221,8279	-
KL (L/mg)	1,166465	-

KF (L/g)	-	101,6481
n	-	2,5463
R2	0,9951	0,8371



(a) **(b)**

Figure 2. (a) Langmuir Isotherm Equation Curve; **(b)** Freundlich Isotherm Equation Curve

From Table 2 and Figure 2, the adsorption process using the Langmuir isotherm produces R2 0.9951, qm of 221.8279 mg/g and KL of 1.166465 L/mg. Parameters qm is a constant indicating the solute adsorbed at the time the adsorbent mass is in a saturated state or exhibits single-layer adsorption (monolayer) or in other words qm is the maximum adsorption capacity an adsorbent with units of mg/g. Langmuir adsorption constant (KL) indicates the degree of adsorbate-adsorbent interaction. KL has a higher value shows a strong adsorbate-adsorbent interaction while the KL value is smaller exhibits a weak interaction between the adsorbate molecule and the surface adsorbent. Once the pollutant occupies the site, no further adsorption takes place can happen on that site. There is no interaction between the molecules adsorbed on the site neighbors, the adsorption on the surface is localized, meaning that the atoms or adsorbed molecules are adsorbed at definite sites and are localized (Langmuir, 1917).

The coefficient can be determined Freundlich (KF) and also the intensity coefficient value (n) of the adsorbent. The adsorption coefficient (KF) can be used as an indicator of adsorption capacity and n is the adsorption intensity. A KF value of 101.6481 L/g was obtained, and a value of n of 2.5463. The Freundlich isotherm describes adsorption as reversible and not limited to the formation of single layers. In general, the higher the value of K_F the higher the adsorption capacity (Malik, 2003). One of the constants Another Freundlich constant is n. Adsorption intensity (n) is a measure of deviation of adsorption linearity which is generally used to determine the rate the truth of an adsorption. If the value for n = 1 then adsorption occurs is linear. If the value for n < 1 then the adsorption process is a process chemical adsorption, but if the value for n > 1 then the adsorption is physical adsorption (Özcan et al., 2005).

Kinetics adsorption

Pseudo-first-order kinetics assumes that the kinetics is affected by One of the reactants is the concentration of the adsorbate. Pseudo first order assumes that the adsorbate concentration is excess compared to the number of available active sites on the adsorbent surface. Lagergren presented the pseudo first order reaction model expression (PFO) as follows:

$$\ln (q_e-q_t)= \ln q_e-k_1 t \tag{4}$$

Where qe and qt are the amount of adsorbate adsorption per mass of adsorbent on equilibrium and at each time t (min), and k_1(min-1) is the rate constant PFO equation. First-order pseudo-kinetics assumes that the kinetics is affected by one of the reactants, namely the concentration of the adsorbate. To determine the equation linear by plotting the value of ln (qe-qt) vs t.

The pseudo second order adsorption reaction (PSO) model expression is obtained from the equation:

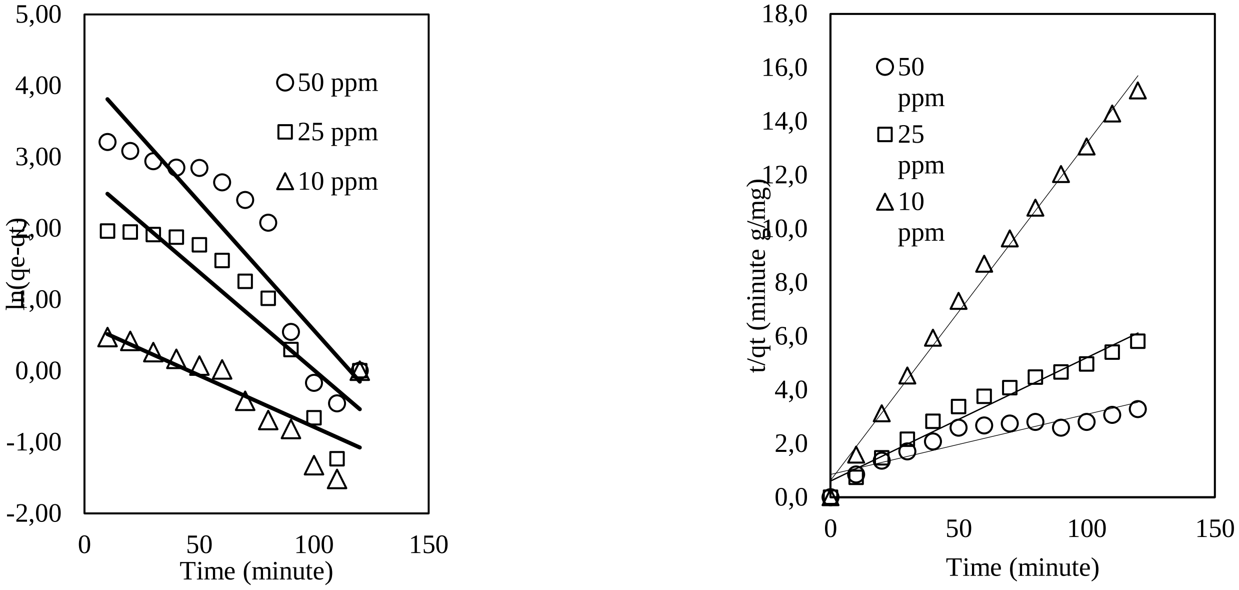
$$\frac{t}{qt}=\frac{1}{k_2qe^2}+\frac{1}{qe}t \tag{5}$$

To determine the linear equation by plotting the values of t/qt vs qe (Ho & McKay, 1998), (McKay et al., 1997).

Table 2. Parameters Obtained from The Pseudo First Order Equation

Conc **(mg/L)**	$q_{e,exp}$	$q_{e,\ calc}$	k_1**(1/mg. min)**	R^2
10	7,92084	2,850	0,019	0,6625
25	20,6683	16,996	0,028	0,8373

50	36,5424	55,376	0,034	0,8501



(a) **(b)**

Figure 3. **(a)** PFO Equation Curve; **(b)** PSO Equation Curve

Observations from Table 2 and figure 3 indicates that the values of $q_{e,\,calc}$ are much different from $q_{e,\,exp}$. This shows that pseudo-first-order equations cannot well explained the adsorption characteristics of Rhodamine B by activated carbon from molasses. From Table 2 it also informs that the rate constant, k1, increases of 0.019, 0.028 and 0.034 g mg-1min-1 for concentrations of 10, 25 and 50 mg/L, p this reveals that the faster adsorption reaches equilibrium with higher initial concentration of Rhodamine B. In many adsorption processes, Lagergren's pseudo-first-order equations are only able to explain in stages the beginning of the adsorption process (initial stage) and unable to describe for all contact time (Muhammad, 2019).

Table 3. Parameters obtained from the pseudo second order equation

Conc **(mg/L)**	$q_{e,exp}$	$q_{e,\,calc}$	k_2	R^2
10	7,920	8,142	0,01754	0,995
25	20,668	23,141	0,002247	0,9658
50	36,542	53,895	0,000294	0,8249

The observation results in Table 3. show that there has been an increase the value of qe and a decrease in the value of K. This is in line with the research which states that together an increase in concentration will lead to an increase in the value of qe and a decrease the value of k_2 caused by adsorption stopping resistance to higher dye concentrations (Gad & El-Sayed, 2009). For the application of pseudo-second-order kinetic models the correlation coefficient R^2 must be high enough and qe, $_{exp}$ must be close enough to $q_{e,\,calc}$ (Muhammad, 2019).

Intraparticle Diffusion

Dynamic adsorption data can be used to identify steps rate-controlling step in the adsorption process (Arasteh et al., 2010). Adsorption of sorbate in sorbents takes place in several steps, involving the transport of solute molecules from the solute phase to the liquid phase. surface of solid particles (film diffusion) and diffusion of dissolved molecules into the interior of the pores, which is usually a slow process. The intraparticle diffusion model is based on the theory proposed by Weber and Morris (Weber & Chakravorti, 1974) will produce the equation following:

$$q_t = k_{id}t^{0,5} \tag{6}$$

Where qt (mg/g) is the amount adsorbed at time t, kid (mg/g.min0.5) is the intraparticle diffusion rate constant

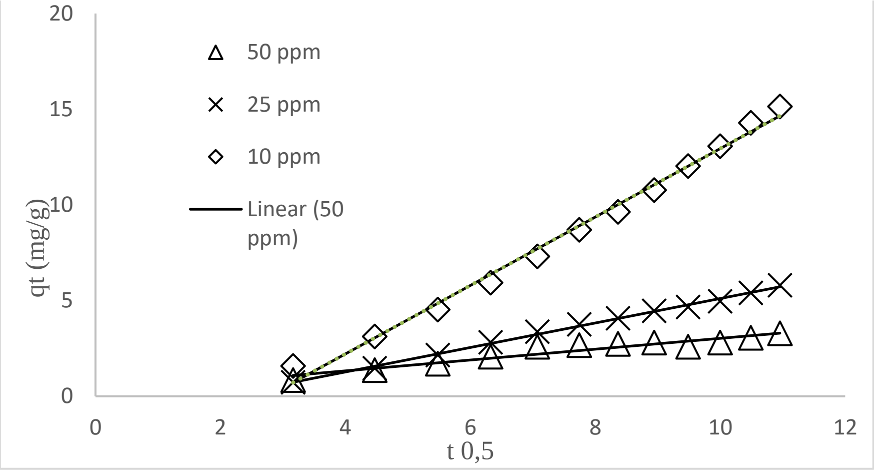


Figure 4. Intraparticle Diffusion Curve

The uptake of RhB onto activated carbon from molasses depends on both film diffusion and intra-particle diffusion, and which is faster will control the overall rate of transfer. Thus, the concentration of adsorbed RhB, qt (mg g−1) is plotted against the application time of the Weber-Morris Equation as shown in Figure 4. According to the intra-particle diffusion model, the linear plot shows the rate controlled by intra-particle diffusion. In a well-stirred batch system, external diffusion resistance is much reduced. Therefore, intraparticular diffusion with adsorption is more likely to be the rate controlling step. At certain time limits for intraparticle diffusion as illustrated in Figure 4. curve shows linear characteristics.

Tabel 4. Intraparticle diffusion parameter

Co (mg/L)	k_{id}	R^2
10	0,213519	0,9621
25	1,079217	0,8999
50	3,515795	0,9402

The intraparticle diffusion parameter, k_{id}, for this region is determined from the slope plot of q versus $t^{0.5}$ with varying adsorbate concentrations. The equation value obtained is y = 0.2135x + 5.46 for an initial concentration of 10 ppm, y = 1.0792x + 8.49 for an initial concentration of 25 ppm, and y = 3.5158x - 1.9075 for an initial concentration of 50 ppm. Data obtained from table 4.14, the diffusion rate, k_{id}, is in the range of 0.213-3.515 mg g−1 min−0.5 with the R^2 value being between 0.8999-0.9621. It was found that the kid value increased with increasing adsorbate concentration, which is in line with research conducted by (Wu et al., 2009). However, the linear plot at each concentration does not pass through the origin. This suggests that intra-particle diffusion is not just a rate-controlling step (Özer et al., 2007).

Conclusions

Adsorption process of Rhodamine B dyes by activated carbon adsorbents from molasses follows the Langmuir isotherm model with a correlation level of R^2 is 0.9951 with a q_{max} of 221.82 mg/g. Adsorption kinetics of Rhodamine B dye by adsorbent activated carbon from molasses has a tendency to match pseudo second order equations get the value of the correlation coefficient (R^2) between 0.8249-0.995 with the values qe, $_{exp}$ and $q_{e,\ calc}$ have only slight differences. The reaction rate for this model was obtained between 0.000294-0.17537 g/mg min. The linear plot at each concentration does not pass through the origin. This suggests that intra-particle diffusion is not just a rate-controlling step. Therefore it can be concluded that Molasses Activated Carbon (MAC) has the potential to become an adsorbent for the adsorption of Rhodamine B dyes.

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