ADSORPTION MALACHITE GREEN ON NATURAL ZEOLITE

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Abstract

A natural zeolite was employed as adsorbent for reducing of malachite green from aqueous solution. A batch system was applied to study the adsorption of malachite green in single system on natural zeolite. The adsorption studies indicate that malachite green in single component system follows the second-order kinetics and the adsorption is diffusion process with two stages for malachite green. Malachite green adsorption isotherm follows the Langmuir model.

Keywords: *adsorption, kinetics, natural zeolite*

Abstrak

Zeolite Alam sebagai absorben untuk mengurangi Malachite Green dari larutan. Studi penyerapan Malachite Green pada sistem tunggal pada Natural Zeolite dilakukan pada sistem tumpak bath. Studi adsorpsi mengindikasikan bahwa malachite green pada single componen adalah kinetik berorde dua dan proses diffusi adsorpsi malachite green adalah dua langkah. Adsorpsi isotherm Malachite green mengikuti model Langmuir.

Kata kunci : *adsorpsi, kinetik, zeolite alam*

INTRODUCTION

Wastewater from textile and dyeing industries contains malachite green. Malachite green is important pollutants, causing environmental and health problem to human being and aquatic animals. Removal of malachite green from wastewater can be achieved by several techniques, such as precipitation, flocculation, adsorption, ion exchange, and membrane separation. Adsorption in believed to be the simplest and most cost-effective technique.

Malachite green is toxic chemical primarily and is subsequently used to treat parasites, fungal infections, and bacterial infection in fish and fish eggs (Mittal *et al*, 2006). Malachite green can be named as 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N dimethyl-anline)(http://www.aquariumpros.ca/forums/showthread.php?p=191402, 2006). Alternatively, the other name is aniline green, basic green 4, diamond green B, or victoria green B.

Zeolite is a group of hydrate aluminosilicates of the alkaline earth metal (http://www.flyash.info/2003/82doc.pdf, 2006). Zeolite formed in nature million of years ago, that is formed when volcanoes erupted huge amount of ash-alumuniumsilicates of alkaline and alkaline earths. The characteristic of a zeolite is based on temperature, geographic location, and ash/water composition. The most important natural zeolite is clinoptilolite. In the past year, natural zeolite has been explored as effective adsorbent for removal of various dyes (Meshko *et al*, 2001; Arinagan *et al*, 2003; Balkose *et al*, 1996; Wang *et al*, 2006)

In this paper, we report an investigation of single-component adsorption equilibrium isotherms, dynamic adsorption, and kinetic adsorption. The investigation of adsorption is very important to optimize the design of zeolite based on ion exchange reactor.

FUNDAMENTAL

The adsorption equilibrium (q_e) is the amount of adsorbed associated with a unit weight of solid adsorbent and residual concentration of adsorbed in the fluid phase.

In order to investigate the adsorption process of malachite green on zeolite is with two kinetic models used. The models are Pseudo-first-order and Pseudo-second-order models.

The pseudo-first-order equation is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

After integration, the integrate form of equation (1) becomes:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

where q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and time t (h), respectively, and k_1 is the rate constant of pseudo-first-order adsorption (h^{-1}).

The pseudo-second-order kinetic model is

$$\frac{dq_e}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

The integrated form of equation (3) becomes:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where k_2 is the rate constant of pseudo-second-order adsorption (mol/g h) and $h = k_2 q_e^2$, where h is the initial adsorption rate (g/mol h).

The rate parameter for intra particle diffusion is calculated using the following equation:

$$q_t = k_p\left(t^{1/2}\right) \quad (5)$$

Where k_p is the intra particle diffusion rate constant.

METHODOLOGY

Material and Chemical

Hard rock zeolite sample (mordenite type) from Baturaja - South Sumatera was sieved, air-dried, bulked into 0.5-2 mm particle size, and evaluated for their ability to remove Malachite Green.

Adsorption Test

The adsorption tests were performed by batch technique at 30°C. For the dynamic adsorption studies in single component system, a series of 250 mL flask were used and each flask was filled with zeolite at varying mass loading (1, 1.5, and 2 g/L). The concentration of Malachite Green is 20 ppm. The agitation was 100 rpm in an orbital shaker and the samples were taken out at a given time interval for analyses. The decreasing of Malachite Green caused by adsorption on natural zeolite is calculated by Spectronic 20 Genesys Spectrophotometer at λ_{max} 617 mm.

RESULTS AND DISCUSSION

Dynamic Adsorption

Figure 1 is the dynamic adsorption of malachite green on natural zeolite at different mass of zeolite. It can be seen that three mass of zeolite show different concentration rate. The adsorption of 2 gram will be faster to reach equilibrium at around 200 h while it will take a longer time (260 h) to arrive at the equilibrium for 1.5 gram and 2 gram.

As seen from Figure 1 that adsorption process will be influenced by the amount of natural zeolite on the basic dye. The adsorption rate at zeolite of 2 gram is higher than 1.5 and 1 gram in which the concentration of malachite green decrease in solution. In this case is caused the adsorption rate of the dye increases with increase for zeolite from 2 to 1 gram.

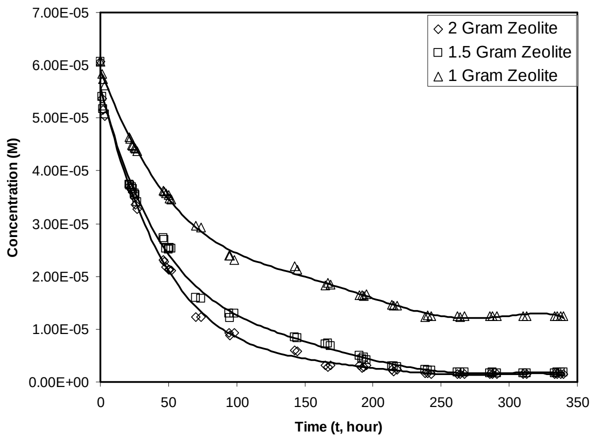

Figure 1. Concentration of Malachite Green on Natural Zeolite (T = 30 °C)

Adsorption Kinetic

First, in Figure 2 is calculated with plotting ln(q_e-q_t) versus time for the pseudo-first-order kinetic given in equation 2. The calculated kinetic parameters are given from this plot and it can be seen in Table 1, respectively. As seen that, the first order kinetic line does not straight line but also the correlation coefficient are much lower (0.8268, 0.7994 and 0.6311). The calculated q_e does not agree very well with the experimental data (q_{eexp}).

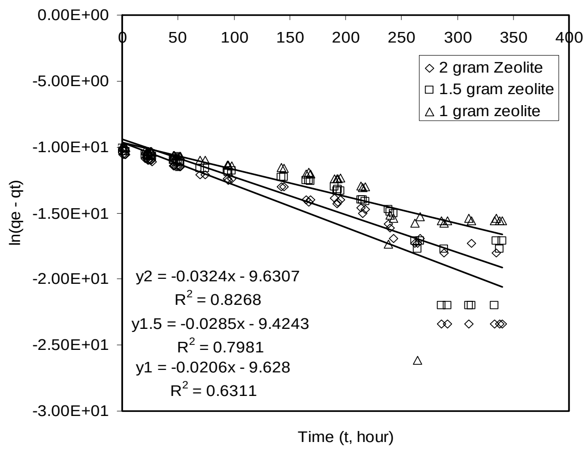

Figure 2. The pseudo-first-order kinetic of Malachite Green adsorption on natural zeolite (T = 30°C)

Second, the plot of (t/q_t) versus time for the pseudo-second-order kinetic given in equation 4 shown in Figure 3 was describe at different mass of zeolite. The q_e and k_2 value were determined from slope and intercept of this plots, respectively. These values in table 2 for second-order model resulting value of R^2 are close to 0.999 in all case. Also the calculated q_e is much close to the experimental value. These indicate that the adsorption perfectly agree with pseudo-second-order reaction. The investigation is similar with investigate two active carbon prepared from Tuncbilek lignite to consider kinetic adsorption of malachite green (Onal *et al*, 2006).

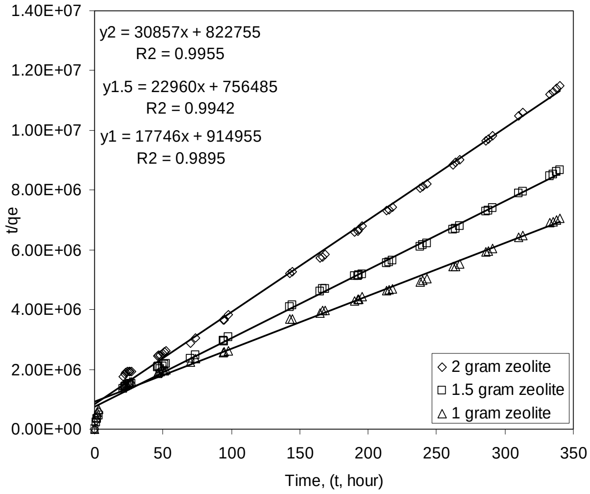

Figure 3. The second-order kinetics of Malachite Green adsorption on natural zeolite (T = 30°C)

Third, from the plots q_t versus $t^{1/2}$ can be determined the intra particle diffusion rate shown in Figure 4. The first linier stage is attributed to external surface adsorption and the second one is intra particle diffusion process. Our previous investigations of basic dyes adsorption on zeolite also indicate a two-stage diffusion process (Wang and Zhu, 2006; Wang *et al*, 2006). This step is similar results with previous study.

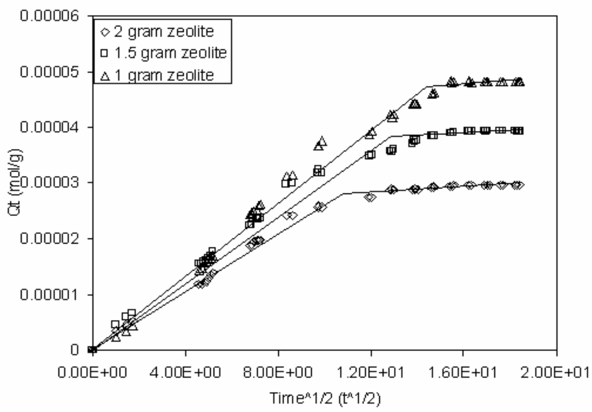

Figure 4. Intra particle diffusion modeling of malachite green adsorption on natural zeolite (T = 30°C)

Adsorption Equilibrium

To optimize the design of an adsorption system for the adsorption of adsorbates, the equilibrium adsorption isotherm is fundamental in describing adsorption capacity behavior between solute and adsorbent.

Freundlich proposed the equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Where q_e is the equilibrium concentration on adsorbent (mol/g), Ce is the equilibrium concentration in solution (mol/l) and K_F (l/g) and n are the Freundlich constants characteristic of the system, indicators of adsorption capacity and reaction energy, respectively.

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Langmuir equation:

$$q_e = \frac{K_L \cdot q_{max} \cdot C_e}{1 + K_L \cdot C_e} \tag{10}$$

Where q_e is the equilibrium concentration on adsorbent (mol/g), Ce is the equilibrium concentration in solution (mol/l) and K_L is the Langmuir adsorption constant (l/mol) which relates to the adsorption energy.

Equation can be treated as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot K_L} + \frac{C_e}{q_{max}} \tag{11}$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L \cdot q_{max}} \cdot \frac{1}{C_e} \tag{12}$$

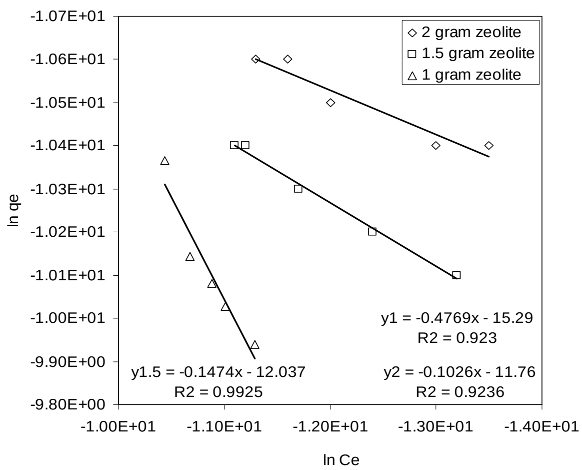

Figure 5. Freundlich isothermal plots for the removal of malachite green on natural zeolite (T = 30°C)

Figure 5 shows that the plot of ln q_e against ln C_e for the Freudlich isotherm testing. Similarly, the plot of Ce/qe versus Ce in Figure 6 tested Langmuir isotherm. The non-linier R^2 values are based on the actual deviation between the experimental points and the theoretically predicted data points are a better correlation and it can be shown in Table 2. Based on the computational outputs, it can be said that the adsorption on natural zeolite is complied with the adsorption theory. This outcome is expected because the assumption that in Freundlich and Langmuir isotherm concept is satisfy the real situation of the system.

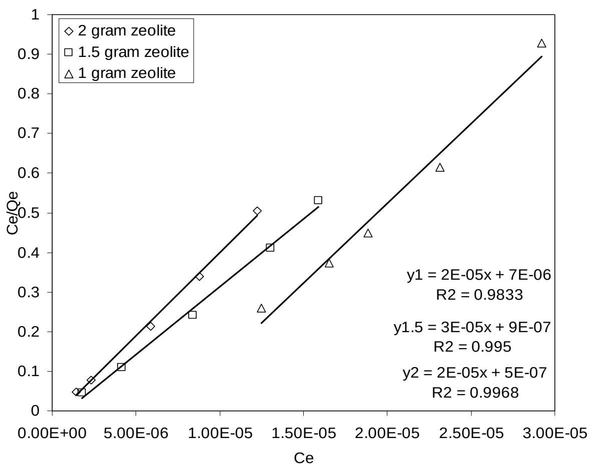

Figure 6. Langmuir isothermal plots for the removal of malachite green on natural zeolite (T = 30°C).

As can be seen, the experimental Langmuir isotherm data is better than the Freundlich isotherm for malachite green on all three adsorbents. The values of parameters for both of isotherm data are given Table 2.

Previous study has been reported that characteristic adsorption of malachite green on Langmuir is satisfactory fit to experimental data (Rahman *et al*, 2005)

The thermodynamic data such as adsorption energy can be obtained from Langmuir equation as follows:

$$\Delta G = -RT \ln K_L \tag{13}$$

K_L is a constant.

The Gibbs free energy of adsorption of malachite green as calculated from the Langmuir constant, K_L was found to be in Table 2, respectively. The energy gibbs of adsorption for malachite green on zeolite of 2, 1.5 and 1 gram was found to be -9.29 x 10^3 kJ/mol, -8.84 x 10^3 kJ/mol, and -8.44 x 10^3 kJ/mol. The same values for all adsorbents indicate that the adsorbents could be used for the malachite green from aqueous solution.

CONCLUSION

The conclusions that can be drawn from the results of this research are natural zeolite was successfully used as adsorbent for removal of malachite green and adsorption of basic dye increased with the amount of zeolite particle from 2, 1.5 and 1 gram in solution. The adsorption capacities are 2.96 x 10^{-5}, 3.93 x 10^{-5} and 4.48 x 10^{-5} mol/g at 2, 1.5 and 1 gram zeolite in 1 liter malachite green. The indication of kinetic show that the adsorptions satisfy with pseudo-second-order reaction with R^2 close to 0.999 and two-step diffusion. The best fits of error analysis of the Langmuir and Freundlich isotherm model show that adsorption isotherm is very well for removal malachite green on natural zeolite, but the experimental Langmuir isotherm data is better than the Freundlich isotherm for malachite green on all three adsorbents. The energy Gibbs of adsorption for malachite green on zeolite of 2, 1.5 and 1 gram was found to be -9.29 x 10^3 kJ/mol, -8.84 x 10^3 kJ/mol, and -8.44 x 10^3 kJ/mol.

Table 1. Kinetic parameter of malachite green adsorption on natural zeolite (T = 30°C)

Mass (g)	Experimental q_e (mol/g)	First-order kinetics			Second-order kinetics		
		q_e (mol/g)	k_1 (1/h)	R^2	q_e (mol/g)	k_2 (mol/g h)	R^2
2	2.96×10^{-5}	6.56×10^{-5}	0.0324	0.8268	3.24×10^{-5}	1.16×10^{3}	0.9955
1.5	3.93×10^{-5}	8.07×10^{-5}	0.0285	0.7994	4.35×10^{-5}	6.99×10^{2}	0.9942
1	4.84×10^{-5}	6.58×10^{-5}	0.0206	0.6311	5.63×10^{-5}	3.45×10^{2}	0.9895

Table 2. Parameters for adsorption isotherms on natural zeolite (T = 30°C)

Mass (g)	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mol/g)	K_L (l/mol)	R^2	K (mol/g)	1/n	R^2
2	5.00×10^{4}	40.00	0.9968	9.18×10^{-6}	- 0.0884	0.9204
1.5	3.33×10^{4}	33.37	0.995	8.09×10^{-6}	- 0.1217	0.9078
1	5.00×10^{4}	28.57	0.9833	2.28×10^{-7}	- 0.4769	0.923

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