Adsorption of Phenol by Mg/Al Hydrotalcite with Ratio Molar 3:1

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Abstract

The adsorption of phenol from aqueous solution by Mg/Al Hydrotalcite with ratio molar 3:1 was studied in a batch adsorption system. Synthesis of Mg-Al hydrotalcite was carried out using co-precipitation method at constant pH followed by hydrothermal treatment at 65°C for 4 days. Phenol removal is pH dependent and the optimum adsorption was observed at pH 5.0. The adsorption rate was established the equilibrium at 120 min and it followed pseudo second order with adsorption rate constant was $4.614 \cdot 10^{-5}$ $mM^{-1} \cdot min^{-1}$. The maximum adsorption capacities abtained from the Langmuir model was 39.063 $mg \cdot g^{-1}$ at room temperature.

Keyword: adsorption, phenol, Mg/Al hydrotalcite

Introduction

Hydrotalcite is a compound that is structurally similar to brucite characteristics and it has a positive charge at the surface (Mills et al., 2012). According Bejoy (2001), hydrotalcite has the general formula as $[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{b+}[A^{n-}_{b/n}] \cdot mH_2O$ where M^{z+} is a divalent cation or a monovalent and A^{n-} is the anion that is on interlayer, while M^{3+} is a trivalent cation that is isomorphous. Methods of synthesis of hydrotalcite can be through the method of coprecipitation, hydrothermal reaction, cohydroxilation MgO and $Al(OH)_3$ (Arruda et al., 2013), sol-gel (Paredes et al., 2006), microwave irradiation, the hydrolysis of urea (Hibino and Ohya, 2009), the steam activation and ion exchange (Tamura et al., 2006).

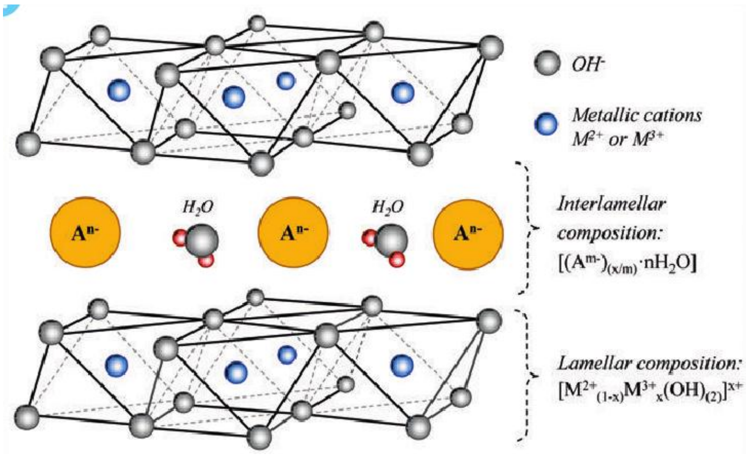

Figure 1 Hydrotalcite structure (Arruda et al., 2013)

Various methods have been developed to reduce the impact of pollution in the environment, such as ion exchange, reverse osmosis, solvent extraction, coagulation, and adsorption. One of the most effective methods is the adsorption because this method is easy to applied, environmentally friendly, inexpensive, and suitable for low pollutant concentrations (Manohar et al., 2006). The level of efficiency of an adsorption process depends on several factors such as area, pore size distribution, polarity, and the functional group of the adsorbent used (Ewecharoena, et al., 2009). Material of Mg/Al Hydrotalcite has a good effectiveness and efficiency as an adsorbent hazardous waste, large adsorption capacity, as well as a good level of efficiency to be very interesting from an economical standpoint. One of utilization of Mg/Al Hydrotalcite was removal phenol in aqueous solution using adsorption methods.

Experimental Methods

Chemicals

All the chemicals used in the experiment were analytical grade. Mg/Al Hydrotalsite 3:1 was sievied to homogenous of particles. The synthesis of Mg/Al hydrotalcite used $Al(NO_3)_3 \cdot 9H_2O$ (Merck), $Mg(NO_3)_2 \cdot 6H_2O$ (Merck), NaOH (Merck) and Na_2CO_3 (Merck). Phenol solution was prepared by dissolving crystal ofe phenol in double destilled water to yield a stock solution.

Synthesis of Mg/Al Hydrotalcite 3:1

Synthesis of Mg / Al hydrotalcite on this study using coprecipitation method referring to research of Zhao et al. (2003) with ratio molar of Mg/Al is 3:1. Magnesium nitrate hexahydrate and aluminum nitrate nonahydrate dissolved in double destilled water with ratio molar of Mg/Al is 3:1 as much as 100 mL and 1 M, solution is called A solution. Subsequently B solution is 2 M of NaOH solution. Solution A and B were mixed drops by drop until pH 10±0,5 with a speed rate 4 mL/minute under vigorous stirring. Then solution stirred at room temperature for 3 hours.The mother solution was poured into a closed vessel with inner liner of teflon and aged at 65°C for 4 days. The precipitate then was separated by filtering and washed with deionized water and dried 65°C overnight.

The Effect of pH

Phenol solution with the same initial concentration was made by varying the pH of a solution of 2, 3, 4, 5, 6, 7, 8 and 9 by adding a solution of 0.01 M HNO_3 and NaOH 0.01 M. A 10 mL phenol at various pH is contacted with 20 mg of adsorbent. Mixture shaked for 24 hours at room temperature. The mixture is then filtered through 42 Whatman filter paper and a Buchner funnel in order to separate between the filtrate and residue. Concentration of phenol which in the filtrate was analyzed by UV-Vis spectrophotometer.

The effect of variation of contact time

The 20 mg of the adsorbent material is contacted with 10 mL of phenol 100 ppm on optimum pH. Mixture shaked with time variations of 15, 30, 60, 90, 120, 150 and 180 minutes. The mixture is then filtered through 42 Whatman filter paper and a Buchner funnel in order to separate between the filtrate and residue. Concentration of phenol which in the filtrate was analyzed by UV-Vis spectrophotometer.

The Effect of Initial Concentration

A total of 10 mg of the adsorbent material is contacted with a solution of phenol with a concentration of 15, 30, 45, 60, 80 and 120 ppm were made at optimum pH. Mixture shaked for optimum time and then filtered using 42 Whatman filter paper and a Buchner funnel so that it can be separated between the filtrate and residue. Concentration of phenol which in the filtrate was analyzed by UV-Vis spectrophotometer.

Results and Discussion

The Effect of pH

Adsorption of phenol increase in the pH of the medium 2 to 5 and its capacity decreases at pH>5. Structure of Mg/Al hydrotalcite damaged in pH 2 so its material ineffective to adsorp phenol in aqoeous solution. Adsorption ability of Mg/Al hydrotalcite will decrease with the increasing of the pH environment . The increasing pH result the number of OH^- ions in solution is also growing. This causes the competition between ion species between phenolic anion and OH^- ions. Binding site on the surface of the Mg/Al hydrotalcite prefers to bind OH^- ions compared to the phenol anion species because it has smaller radius hydration.

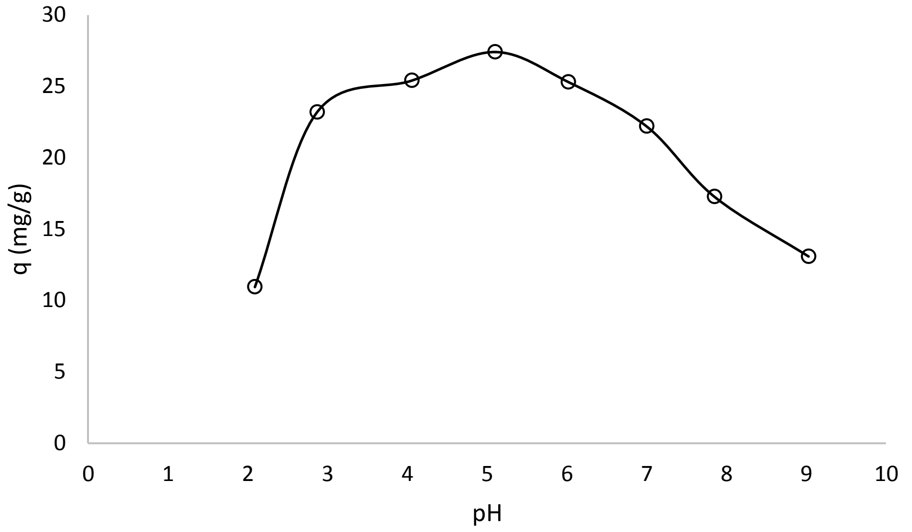

Figure 2 The effect of pH on removal phenol by Mg/Al Hydrotalcite 3:1

The effect of variation of contact time

Effect of contact time on phenol adsorption with Mg / Al hydrotalcite 3 : 1 effective in the first 30 minutes. The results showed that the increasing contact time causes increased adsorption capacity of phenol by Mg/Al hydrotalcite 3:1 and reached equilibrium at the contact time of 120 minutes.

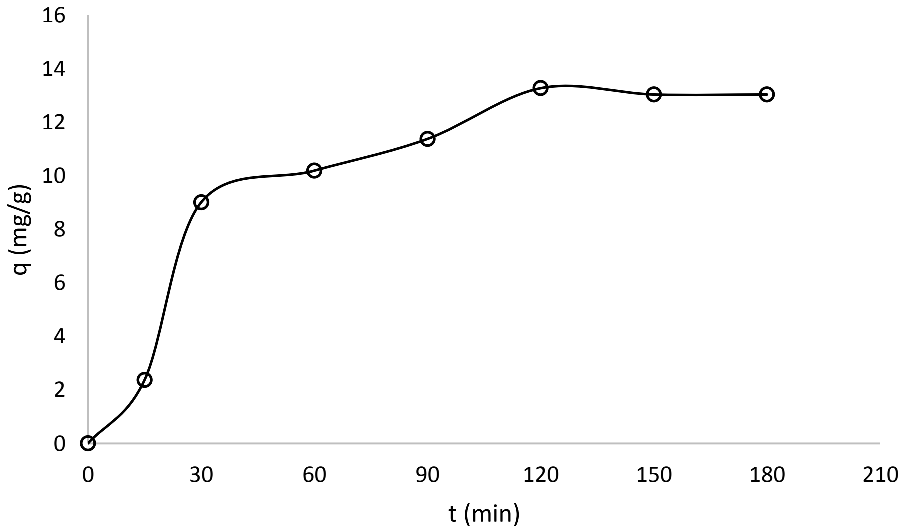

Figure 3 The effect of contact time on removal phenol by Mg/Al Hydrotalcite 3:1

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Results of the study were tested using adsorption kinetics model using first order, second order, pseudo first order and pseudo second order models for sorption processes. The equation can be seen in Table 1.

Table 1 Kinetic models for sorption processes

Model	Equation	Linear Equation	Plot Graphs
1st Order	$-\frac{d[C]}{dt} = k[C]$	$\ln C_e = -K_1 t + \ln C_o$	$\ln\frac{Co}{Ce}$ vs t
2nd Order	$-\frac{d[C]}{dt} = k[C]^2$	$\frac{1}{C_e} = k_2 t + \frac{1}{C_o}$	$\frac{1}{Ce}$ vs t
Pseudo 1st order	$\frac{dq_t}{dt} = k(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{k_3}{2,303} t$	$\log(q_e - q_t)$ vs t
Pseudo 2nd order	$\frac{dq_t}{dt} = k(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_4 q_e^2}$	$\frac{t}{q_t}$ vs t

The data in Table 2 shows that the pseudo second order model is more suitable to describe the adsorption kinetics of phenol with Mg/Al hydrotalcite 3:1. Reaction kinetics model showed that the adsorption rate equal to the square of the concentration of phenolic ion expressed by $(qe – qt)^2$ in the pseudo second order model equation.

Table 2 Kinetic Models of phenol adsorption using Mg/Al Hydrotalcite 3:1

Kinetic Model	**k**		**R^2**
1st Order	min^{-1}	$1.10 \cdot 10^{-3}$	0.704
2nd Order	$mM^{-1}\ min^{-1}$	$0,50 \cdot 10^{-3}$	0.727
Pseudo 1st order	min^{-1}	$2.07 \cdot 10^{-2}$	0.872
Pseudo 2nd order	$mM^{-1}\ min^{-1}$	$4.61 \cdot 10^{-5}$	0.880

The Effect of Initial Concentration

Results of the effect of initial phenol concentration to the adsorption capacity of Mg/Al hydrotalcite 3:1 can be seen in Figure 3. Assessment isotherm models using Langmuir and Freundlich isotherm equations showed in Table 3.

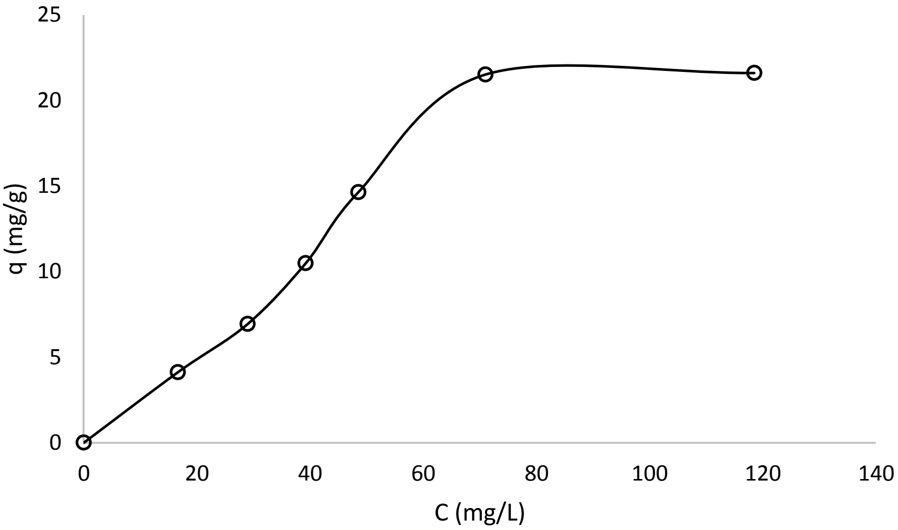

Figure 4 The effect of initial concentration on removal phenol by Mg/Al Hydrotalcite 3:1

Table 3 Isoterm Models Equation

Isoterm	Nonlinear equation	Linear equation	Plot graph
Langmuir	$q_e = \frac{q_{maks} K_L C_e}{1 + (K_L C_e)}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_{maks}} + \frac{C_e}{q_{maks}}$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_F (C_e)^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$

Where C_e is the concentration at equilibrium, q_e is the amount of adsorbed substances and q_{max} is adsorption capacity, K_L is the Langmuir equilibrium constant, K_F is a constant binding energy, which shows affinity or adsorption capacity adsorbent for adsorbate and n are Freundlich constant. Constant of K_F and K_L can be determined from a linear equation, where K_L = 1/(intercept × q_{max}) and q_{max} = 1/slope in the linear equation of Langmuir and K_F =exp (intercept) and 1/n = slope of the linear equation Freundlich isotherm. Isotherm study results of this research can be seen in Table 4.

Table 4 Isoterm Model on removal phenol by Mg/Al Hydrotalcite 3:1

Langmuir Isoterm			Freundlich Isoterm		
K_L (L/mg)	q_{max} (mg/g)	R^2	K_F (mg/g)	n	R^2
0.0195	39.063	0.977	1.02	1.3	0.748

Table 4 shows that the adsorption of phenol using Mg/Al hydrotalcite 3:1 is fitted with the Langmuir isotherm studies were characterized by the determination coefficient in linear equation model of Langmuir greater than Freudlich models. It is stated that the adsorption of phenol using Mg/Al hydrotalcite 3:1 shows that the adsorbate molecules do not interact with one another, all the adsorption takes place by the same mechanism and adsorption only lasted monolayer.

Conclutions

Adsorption of phenol using Mg/Al hydrotalcite with molar ratio of 3:1 effective occurred at pH 5 and optimum contact time of 120 minutes. Adsorption of phenol in accordance with pseudo second order kinetic model and fitted on the Langmuir isotherm with the maximum adsorption capacity of 39.063 mg/g.

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