

THE PERFORMANCE OF SYNTHETIC ZEOLITE COMBINED WITH ACTIVATED CARBON FOR REMOVAL OF LINURON HERBICIDE

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Abstract

This research is to study the efficacy of linuron herbicide removal from wastewater with four adsorbents. These adsorbents were 1) synthetic zeolite NaY combined with activated carbon (SZA) 2) synthetic zeolite NaY with activated carbon and modified with HDTMA surfactant (MSZA) 3) synthetic zeolite NaY (SZ) and 4) synthetic zeolite NaY and modified with HDTMA surfactant (MSZ). The results showed that the adsorption of linuron herbicide of all adsorbents increased rapidly and approach to equilibrium at 24 h. When the amount of adsorbent increased, the adsorption of linuron herbicide also increased. The maximum adsorption efficiency SZA, MSZA, SZ and MSZ were 63.49 %, 77.97 %, 66.57 % and 38.52 %, respectively at a concentration of 2 ppm linuron, 0.1 g. of adsorbents and 24 h. The adsorption isotherm corresponded to Langmuir model. XRD, FT-IR and SEM techniques were use to study the characteristics of these adsorbents. In summary, zeolite synthesis combined with activated carbon (ZSA) has efficiency in adsorbing linuron herbicide and as an alternative to eliminate pesticide, herbicide, organic toxins and other wastes released into the environment.

Keywords: Zeolite, activated carbon, linuron, herbicide, environment

Introduction

Linuron is a type of herbicide, commonly known as “killer grass”. The chemical name is 3- (3, 4-dichlorophenyl) -1-methoxy-1-methylurea. Formulation: $C_9H_{10}Cl_2N_2O_2$. It is a chemical

herbicide of the photosynthetic inhibitors by binding to specific site in chlorophyll. It can kill many weeds and other plants. If there is residue, it will be harmful to consumers and

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mammals. The frightening thing is that only 0.1 percent of the pesticides that will reach the target enemy, but 99.9 percent will contaminate the environment, especially soil and water that affects the ecosystem and food chain.

There are many ways to solve weeds in the environment, such as filtration, coagulation, sedimentation, *bioaugmentation* and adsorption etc. Adsorption is a simple, low-cost and highly effective method (Sadaf and Bhatti, 2104). There are many types of absorbent materials, such as zeolite, perlite, bentonite, silica, minerals clay and activated carbon (Krysztalkiewicz *et al.*, 2002; Woolard *et al.*, 2002; Wang *et al.*, 2004; Sirival, 2015). In this research, zeolite and activated carbon will be studied. Zeolite is a crystalline structure formed by the bonding of tetrahedral silicate and alumina units. The internal structure of the zeolite is porous and the cavity is large enough for the cation exchange, catalysis and adsorption etc. (Chutia *et al.*, 2009). Activated carbon is a product that is produced using raw materials containing carbon and hydrogen as the main component through the activation process until getting the black product. Activated carbon has a porous structure with a high surface area and has the ability to absorb various substances well. From the properties of zeolites and activated carbon, it is an alternative way to treat wastewater caused by the linuron herbicide. Therefore, this research focuses on the synthesis of zeolite combined with activated carbon as an absorbent material to get rid of the residual linuron herbicide in the environment.

Materials and Methods

Synthesis of Adsorbent Materials (SZ)

Zeolite NaY (SZ) was synthesized by hydrothermal reaction from the initial substance between 4.62 mol Na₂O, 1 mol Al₂O₃, 10 mol SiO₂ and 180 mol H₂O. The solution was aged at room temperature for 1 day. After that, make it crystallized by drying at 100°C for 7 h then washed with deionized water until the pH of filtrate became neutral

(pH 6.3). Filtered and eliminate moisture by drying at 110°C for 12 h. Collected samples for further experiments.

Synthesis of Absorbent Materials (SZA)

Zeolite NaY synthesized together with activated carbon (SZA) was synthesized by hydrothermal reaction from the initial substance between 4.62 mol Na₂O, 1 mol Al₂O₃, 10 mol SiO₂, 180 mol H₂O and 2 g of activated carbon. The solution was aged at room temperature for 1 day. After that, make it crystallized by drying at 100°C for 7 h then washed with deionized water until the pH of filtrate became neutral (pH 6.3). Filtered and eliminate moisture by drying at 110°C for 12 h. Collected samples for further experiments.

Preparation of Absorbent Materials (MSZ And MSZA)

Added 100 ml. of 1 ppm HDTMA surfactant in 1.0 g of SZ and SZA synthetic materials. Stirred for 24 h. After that, centrifuge at a speed of 3,200 rpm. Filtered the filtrate and removed moisture by drying at 110°C for 12 h. Collected samples for further analysis.

Adsorption

Adsorption of linuron on four absorbent materials: SZA, SZ, MSZA and MSZ with batch methods. Add 25 ml. linuron to each absorbent material in neutral solution (pH 6.3). After that, centrifuge at a speed of 3,200 rpm for 20 min. Filtered the solution with a filter paper of 45 micron and then analyzed the adsorption efficiency with HPLC. The study of adsorption factors were as follows: 1) Absorption time 3, 6, 12, and 24 h 2) The amount of adsorbent 0.04, 0.06, 0.08, 0.1 g 3) linuron concentration 0.5, 1.0, 1.5, and 2.0 ppm and 4) Langmuir adsorption isotherm.

Characteristics of Adsorbents

Studied the characteristics of adsorbents using XRD, FT-IR and SEM techniques. The XRD analyses of adsorbent material were carried out using Bruker D5005 powder X-ray diffractometer. The X-ray was generated from a Cu K α target with a current of 35 mA and potential of 35 kV. Each diffraction spectrum

was recorded with 2-Theta angle of between 3° to 50° and scan speed of 0.4 degree/0.02 sec. The Infrared spectra (FT-IR) were obtained using a Perkin-Elmer spectrum GX FTIR Spectrophotometer and infrared spectra were taken in the range of mid infrared ($4,000\text{--}650\text{ cm}^{-1}$). Morphology of the materials could be seen through the use of scanning electron microscope (SEM). The observation was done by scanning electron microscope model JSM-

5410LV, HV mode. The micrographs were recorded with an accelerating voltage of 20 kV and 5,000x-8,000x magnification.

Result and Discussion

Synthesis Materials Characterization

The adsorbent materials obtained from the synthesis experiments were identified by using powder X-ray diffraction. Figure 1 XRD pattern exhibited the normal diffraction lines of synthesized SZ is crystalline phase. The intense line at 2θ values of 6.34, 10.18, 11.90, 15.76, 20.46, 23.70, and 27.10 respectively, corresponding to the XRD pattern of JCPDS# 39-0218. while the XRD diffractogram of SZA breaks out from the zeolite NaY crystal structure, since activated carbon is added to the synthesis process.

These explains the collapse of the zeolite structure. The broad peak due to the amorphous phase became more obvious. Explained that the formation of the amorphous phase was attained with the breaks out of the zeolite framework structure.

The IR spectra of synthesized zeolite SZA and SZ were presented in Figure 2. It was found that the strongest vibration at 976 cm^{-1} specified to asymmetric stretch of Si(or Al)-O-Si(or Al), 782 cm^{-1} was symmetric stretch of Si-O-Al (Breck, 1974). The intensity at 3,409-3,413 cm^{-1} were specified to O-H stretch.

The surface morphology of synthesized zeolite SZA and SZ was observed by electron microscope (SEM) (Figure 3). There were small sizes and octahedral shape crystals for SZ material. The SZA cannot determined type of crystal, which consisted with the X-ray analysis results.

Study of Adsorption of Linuron Herbicide

The adsorption of linuron herbicide was carried out under various effects, such as effect of adsorption time, adsorbents dosage in neutral solution (pH 6.3). The amount linuron concentration was determined by HPLC (Figure 4). This adsorption of linuron with the four samples; SZA, MSZA, SZ and MSZ were considered under various influences. It found

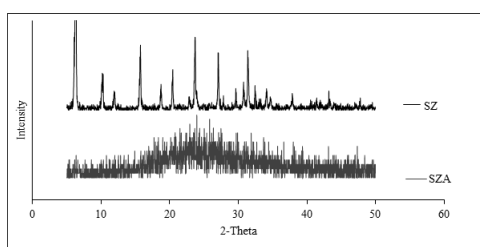


Figure 1. XRD diffraction pattern of synthesized of SZA and SZ

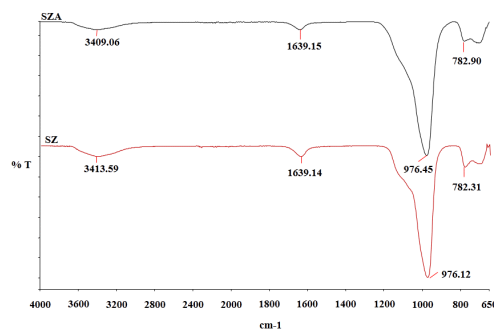


Figure 2. FT-IR spectra of synthesized of SZA and SZ

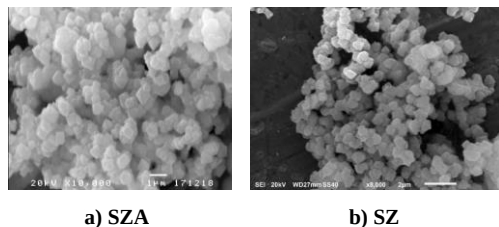


Figure 3. Morphology of synthesized of SZA and SZ

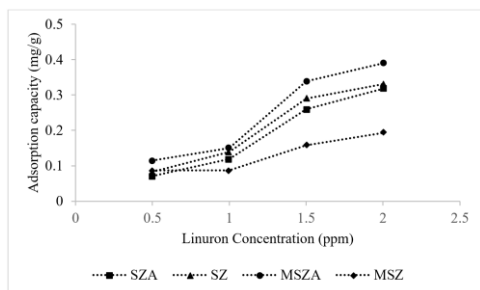


Figure 4. Adsorption capacity of linuron herbicide on 24 h, 0.1 g adsorbents and varied linuron concentration

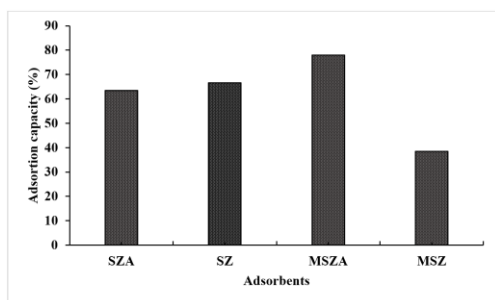


Figure 5. The maximum adsorption capacity of linuron herbicide on 24 h, 0.1 g adsorbents and 2 ppm linuron concentration

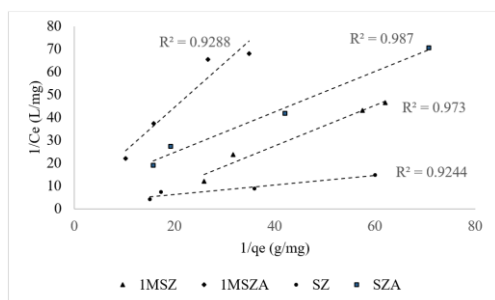


Figure 6. Langmuir adsorption isotherm

the maximum adsorption capacity of SZA, MSZA, SZ, and MSZ were 63.49%, 77.97%, 66.57%, and 38.52%, respectively on 24 h, 0.1 g adsorbents and 2 ppm linuron concentration (Figure 5). Explained that SZA and SZ have

similar efficacy in removing pesticides. At the same time, it was found that removal efficiency of linuron herbicide increased 14.48% when adding HDTMA surfactant (MSZA). This is because the structure of MSZA has a porous of Si(or Al)-O- Si(or Al) structure and the layer of the activated carbon structure. The HDTMA enter into the MSZA framework very much, therefore it absorbed the most linuron herbicide. However, the MSZ has only a porous structure, causing steric effect and HDTMA surfactant block porosity of zeolite (Sirival, 2015).

Study of adsorption isotherm

In this study, the adsorption isotherm was studied at the adsorption time 24 h, linuron concentration 0.5, 10, 1.5, and 2.0 ppm and 0.1 g adsorbents weight. The Langmuir's isotherm which describe the relationship between the concentration of linuron remaining at equilibrium and ability to absorb linuron at a constant temperature was shown in Equation 1-2.

The Langmuir isotherm represents chemisorption and monolayer adsorption. The non-linear form of Langmuir Equation (Leyva-Ramos *et al.*, 2008) is shown in Equation (1) and the linear form in Equation (2).

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m} \frac{1}{C_e} \quad (2)$$

From Langmuir's equation for the Equation (2) q_e is the amount of linuron absorbed per zeolite balance concentration (mg/g). Q_m is the maximum absorption that occurs in a monolayer. (mg/g). C_e is the concentration that the balance of linuron (mg/L) and K_L is the Langmuir constant (L/mg) When writing a graph between $1/q_e$ and $1/C_e$ (Figure 6).

The isotherm constants of adsorption show in Table 1. Considering the correlation coefficient (R^2) is between 0.9244-0.9870. The adsorbent material with the highest R^2 value is

SZA ($R^2 = 0.9870$). The maximum adsorption efficiency of SZA, MSZA, SZ and MSZ are 0.1645, 0.1785, 0.1438, and 0.1282 mg/g, respectively. Therefore, it can be explained that these adsorptions are consistent with the Langmuir equation, which arises from the physical attraction that can be reversed by the highest adsorption occurs on a monolayer.

Table 1. Langmuir isotherm constants for adsorption of linuron

Adsorbents	Langmuir Adsorption Isotherm		
	R^2	Q_m (mg/g)	K_L (L/mg)
SZA	0.9870	0.1645	6.8526
MSZA	0.9288	0.1785	2.8763
SZ	0.9244	0.1438	13.627
MSZ	0.9730	0.1282	8.8109

Conclusions

Adsorbent prepared from the synthesis of zeolite NaY combined with activated carbon (SZA) by hydrothermal method have the efficiency of linuron herbicide adsorption. The SZA adsorption efficiency has 63.49% in 24 h. The amount of adsorbent was 0.1 g. and the linuron concentration was 2 ppm. Moreover, it was found that the adsorption efficiency of linuron increased by 14.48% when the HDTMA surfactant was modified onto the adsorbent. In addition, the experimental results are consistent with Langmuir adsorption isotherm. Therefore, the adsorption of linuron is chemically absorbed which can absorb in monolayer. In summary, zeolite synthesis combined with activated carbon (ZSA) has efficiency in adsorbing linuron herbicide and as an alternative to eliminate pesticide, herbicide, organic toxins and other wastes released into the environment.

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