

## Isotherm study on adsorption removal of Pb (II) by MCM-41 zeolite synthesized from biomass ash

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**Abstract.** This paper focuses on the adsorption of Pb(II) from aqueous solution on zeolite that was synthesized from biomass ash. A synthesized MCM-41 zeolite marked as MCM-41-S9 was studied as adsorbent. Then, adsorption characterization of Pb(II) onto MCM-41-S9 was discussed. Test results showed that optimum conditions for Pb(II) removal were found to be pH 5 to 6, adsorbent dosage 6 g/L of solution and equilibrium time 2 h. The equilibrium adsorption isotherm can be well described by Langmuir adsorption isotherm model. The adsorption capacity of MCM-41-S9 for Pb(II) ions in terms of monolayer adsorption was  $34.33 \text{ mg}\cdot\text{g}^{-1}$  at initial concentration of  $300 \text{ mg}\cdot\text{L}^{-1}$ . MCM-41-S9 was adaptive and efficient to removal Pb(II) in the solutions with lower pH value. The change of entropy ( $\Delta S_0$ ) and enthalpy ( $\Delta H_0$ ) were estimated at  $338.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $96.2 \text{ kJ}\cdot\text{mol}^{-1}$  respectively; The negative value of Gibbs free energy ( $\Delta G_0$ ) indicate feasible spontaneous and endothermic adsorption of Pb(II) on MCM-41-S9. The value of the adsorption activation energy ( $E$ ), calculated using modified pseudo-second-order kinetics model, was  $-9.06 \text{ kJ}\cdot\text{mol}^{-1}$  and testified the reaction was spontaneous, stable and exothermic.

### Introduction

It is widely accepted that bio-fuels combustion does not contribute to the greenhouse effect due to the CO<sub>2</sub> neutral conversion thanks to the renewability of biomass. The focus on bio-energy as an alternative to fossil energy has increased tremendously recently because of global warming problems originating mostly from fossil fuels combustion [1]. The technological disadvantages and environmental risks related to biomass ash have been stated recently. Some environmental risks and health concerns related to biomass ash, such as contamination, leaching characterization, volatilization, retention, capture and immobilization of hazardous elements, inhalation, disposal, have become more important and urgent [2-4]. Rice husks ash is a solid waste product from the power generating industry which is suitable for recycling. The silica in rice husk is amorphous and transforms to crystalline silica when it is heated at high temperatures. Pure rice husks ash is used as silica resource for the production of silicon based materials with industrial and technological interests [5, 6]. It is known that extensive research was carried on zeolite synthesis especially made from rice husks ash [7, 8]. Its unique pore structure has excellent shape selectivity, while the character to develop adsorption ability makes it an interesting material for adsorption removal pollutants from aqueous solutions.

In this study, biomass ash from biomass-fired power plant, which typically utilized agricultural and forest residues mixtures as fuel, was chosen as raw materials to synthesize MCM-41 zeolite. The effect of Na<sub>2</sub>O/SiO<sub>2</sub> ratio on MCM-41 preparation and physical properties and crystallinity of the synthesized zeolites are investigated. adsorption characterization of lead onto synthesized zeolites was discussed in batch adsorption tests. Adsorption isotherm and kinetics were described as well.

## Materials and Methods

**Materials.** Biomass ash (obtained from local biomass-fired power plants), analytical sodium hydroxide, aluminum sulfate, lead nitrate, cetyltrimethyl-ammonium-bromide (CTAB), Polyethylene Glycol (PEG-2000) were used in this study. Biomass ash with heat treatment and aluminum sulfate were used as Si and Al source, respectively. Concentrated sulfuric acid was used for adjusting the pH. Different parameters that were studied to increase crystallinity and to decrease the crystal diameter of MCM-41 were the effect of  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio. Dry biomass was milled and sieved to eliminate the larger particles. Samples of ash were calcined at  $800^\circ\text{C}$  for 3 h. The chemical compositions of Biomass ash with and without heat treatment are listed in Table 1.

Oxide	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{P}_2\text{O}_5$	$\text{Na}_2\text{O}$	$\text{SO}_3$	LOI (Loss on ignition)
Original biomass ash [wt.%]	72.25	1.12	1.28	3.34	2.32	2.09	0.75	0.82	2.11	12.63
Biomass ash with heat treatment [wt.%]	86.52	1.23	1.45	1.25	2.27	2.28	0.85	0.98	1.78	0.88

Table 1 Chemical composition of biomass ash without and with heat treatment at  $800^\circ\text{C}$  for 3 h.

**Samples Synthesis and Preparation.** In this study alkali-activated hydrothermal synthesis method was used to prepare objective zeolites. The hydro-gels of the oxide molar compositions were prepared for the synthesis of MCM-41 zeolite by using the molar ratios provided in Table 2. The detailed procedures of synthesis were described as following: (1) heat treatment biomass ash of 4 g was added into 200 ml Erlenmeyer flask which contained moderate de-ionized water; (2) a specific amount of NaOH was added to silica. Solutions were stirred and heated at  $85^\circ\text{C}$  until a clear solution was reached; meanwhile, CTAB was dissolved in a little amount of de-ionized water with heating at  $50^\circ\text{C}$  for 15 min. The solution of CTAB was added to that of sodium silicate solution while stirring for 10 min. Model PEG-2000 (1 mL) was added into mixed solutions as a mobilizing agent. The aluminum sulfate was dissolved in a small amount of de-ionized water while adding 0.1 mL concentrated  $\text{H}_2\text{SO}_4$  with stirring until reaching a clear solution. At last the aluminum sulfate solution was added into mixed solution prepared above by stirring for 1 h and adjusting pH of solution to 12. The final mixed solution was hydro-thermally treated at  $120^\circ\text{C}$  in an oil bath, using stainless steel autoclaves, for 2 days. The autoclaves were removed at the specified time from the oil bath and cooled under room temperature. The solid product was filtered and washed with distilled water until the pH of the filtrate dropped to 7.5. The products were dried at  $110^\circ\text{C}$  for 2 h, and then calcined at  $550^\circ\text{C}$  for 3 h in muffle furnace. After all of steps, MCM-41 zeolite samples were prepared by milling and sealing.

Table 2 Various oxide molar ratios for synthesis MCM-41 zeolites.

Samples	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{CTAB}/\text{SiO}_2$	$\text{PEG-2000}/\text{SiO}_2$	$\text{H}_2\text{O}/\text{SiO}_2$
S1	1.43	5	0.4	—	28.6
S2	1.43	5	0.4	—	57.2
S3	1.43	30	0.4	—	57.2
S4	1.0	5	0.4	—	57.2
S5	0.2	5	0.15	—	40
S6	0.2	15	0.15	—	40
S7	0.5	30	0.15	—	40
S8	0.2	30	0.15	—	40
S9	0.3	30	0.15	—	40
S10	0.3	30	0.14	0.01	40
S11	0.2	30	0.14	0.01	40

S12	0.5	30	0.14	0.01	40
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**Adsorption Characterization.** A series of Pb(II) solutions with different concentrations were prepared by dissolving a known amount of lead nitrate into 250 mL of de-ionized water in different transparent containers. Adsorption experiments as a function of pH, contact time and concentration were conducted in a borosilicate reaction vessel at controlled room temperature under nitrogen atmosphere. The concentration of metal ions was determined by using a Varian flame atomic absorption spectrophotometer.

**Adsorption Models and Equations.** Eq. 1 gives the the linear form of Langmuir model [9]:

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

For the Langmuir model, the constant  $b$  ( $L \cdot mg^{-1}$ ) is related to the energy of adsorption;  $C_e$  ( $mg \cdot L^{-1}$ ), the equilibrium concentration of the adsorbate in solution;  $q_e$  ( $mg \cdot g^{-1}$ ), the amount of adsorbed adsorbate on the adsorbent surface at equilibrium and the constant  $Q_m$  ( $mg \cdot g^{-1}$ ), represents the maximum binding at the complete saturation of adsorbent binding sites.

Freudlich model [10] and its linear form:

$$q_e = K_F C_e^{1/n} \quad (2)$$

$K_F$  and  $n$  are the Freundlich adsorption isotherm constants characteristic of the system.  $K_F$  and  $n$  are indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively.

In thermodynamics equation, change of Gibbs free energy was calculated by Eq. (3), and change of entropy and heat of adsorption are calculated and estimated by Eq. (5):

$$\Delta G^0 = -RT \ln K_e \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (4)$$

$$\ln K_e = -\Delta H^0 / RT + \Delta S^0 / R \quad (5)$$

Activation energy in process of adsorption can be calculated by Arrhenius equations:

$$k_1 = k_0 \exp\left(\frac{-E}{RT}\right) \quad (6)$$

$$\ln k_1 = \ln k_0 - \frac{E}{RT} \quad (7)$$

where, at equilibrium for all equations,  $\Delta G_0$  is change of Gibbs free energy ( $kJ \cdot mol^{-1}$ ),  $\Delta S_0$  ( $J \cdot K^{-1} \cdot mol^{-1}$ ) and  $\Delta H_0$  ( $kJ \cdot mol^{-1}$ ) are change of entropy and heat of reaction;  $K_e$  means equilibrium distribution constant;  $k_1$  is the pseudo-second-order kinetic model rate constant which was not calculated in this study;  $k_0$  is the pre-exponential factor;  $E$  ( $kJ \cdot mol^{-1}$ ) means activation energy  $T$  (K) is absolute temperature, and  $R$  ( $8.314 J \cdot K^{-1} \cdot mol^{-1}$ ) is universal gas constant.

## Results and Discussion

**SEM and TEM Analysis.** Fig. 1 shows the SEM images of synthesized MCM-41 zeolite obtained from sample S9 which was marked as MCM-41-S9. From Fig. 1 (a) and (b), it can be observed the uniform particles and tidy structure. This indicated and testified the procedure of synthesis mechanism by observing synthesized products crystalline microstructure in Fig. 1. Those hierarchical and tidy mesoporous structures were observed from TEM images in Fig. 1 (c) and (d). Aperture of synthesized mesoporous materials was about 2 to 5 nm. The dark section in images stated that random porous structure existed and synthesized MCM-41-S9 zeolite was inferior to MCM-41 type zeolite made from pure raw materials.

**Adsorption isotherm study.** Adsorption of Pb(II) from aqueous solutions into MCM-41-S9 was measured at a contact time of 2 h and pH=6. Three different initial Pb(II) concentrations were considered ( $20-300 mg \cdot L^{-1}$ ) at an adsorbent dose of  $6 g \cdot L^{-1}$ . The amount of adsorbed Pb(II) onto (into) the MCM-41-S9 at equilibrium were studied and plotted in Fig. 2 as a function of the equilibrium

concentration of Pb(II). In this study, data obtained from Pb(II) adsorption isotherm tests were fitted well with the Langmuir isotherm model as described in Eq.(1). This implied that the adsorption process of MCM-41-S9 was consistent with those obtained from the Langmuir isotherm equation and confirmed that the Pb(II) adsorption onto MCM-41-S9 belonged to homogeneous monolayer adsorption type. The values of  $Q_{m,cal}$  ( $Q_m$  value calculated by Langmuir isotherm equation) and  $b$  in the range of studied initial concentration were found to be  $36.48 \text{ mg}\cdot\text{g}^{-1}$  and  $0.0817 \text{ L}\cdot\text{mg}^{-1}$ , respectively. At the initial concentration of  $300 \text{ mg}\cdot\text{L}^{-1}$ , the  $Q_{m,exp}$  ( $Q_m$  value tested from experiment) was  $34.33 \text{ mg}\cdot\text{g}^{-1}$ . the value of  $Q_{m,cal}$  was close to that of  $Q_{m,exp}$ , which indicated that the maximum adsorption capacity can be determined by fitting Langmuir isotherm equation.  $K_F$  and  $n$  was calculated as 6.4 and 2.71. The value of  $R^2$  of Langmuir and Freundlich isotherm fitting equations were 0.9627 and 0.8852, respectively. It indicated that the equilibrium adsorption isotherm was better described by Langmuir adsorption isotherm model.

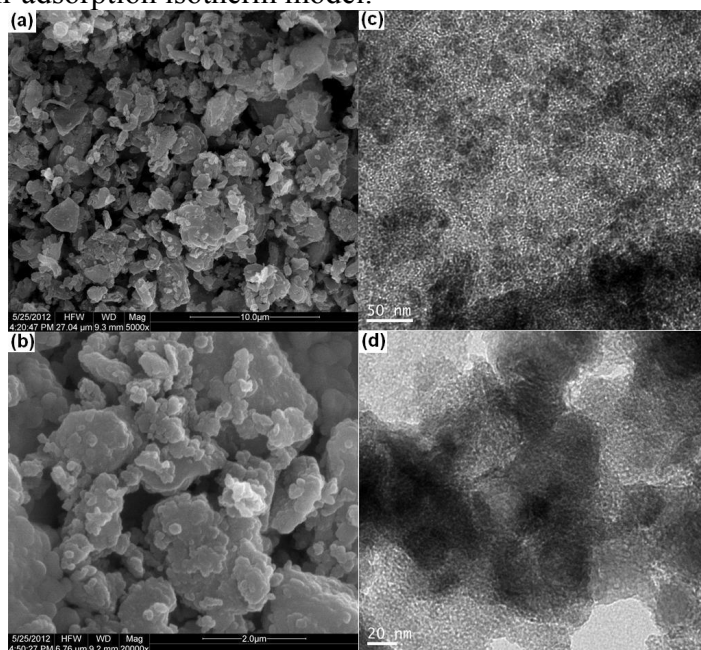


Fig. 1. SEM and TEM images of MCM-41-S9: (a) (b) SEM images at different magnification factors; (c) (d) TEM images for mesoporous structure.

**Effect of pH on adsorption.** The effect of initial pH on adsorption of Pb(II) was studied at room temperature, constant initial Pb(II) concentration of  $20 \text{ mg}\cdot\text{L}^{-1}$ , adsorbent dose of  $6 \text{ g}\cdot\text{L}^{-1}$  and contact time of 2 h. Fig. 3 shown the effect of pH on the adsorption of Pb(II) onto MCM-41-S9. With the increase of pH value, adsorption capacity increased. In the studied pH change range, the maximum uptake of the Pb(II) was obtained at pH value from 4 to 5. This indicated that MCM-41-S9 was adaptive and efficient to removal Pb(II) in the solutions with lower pH value.

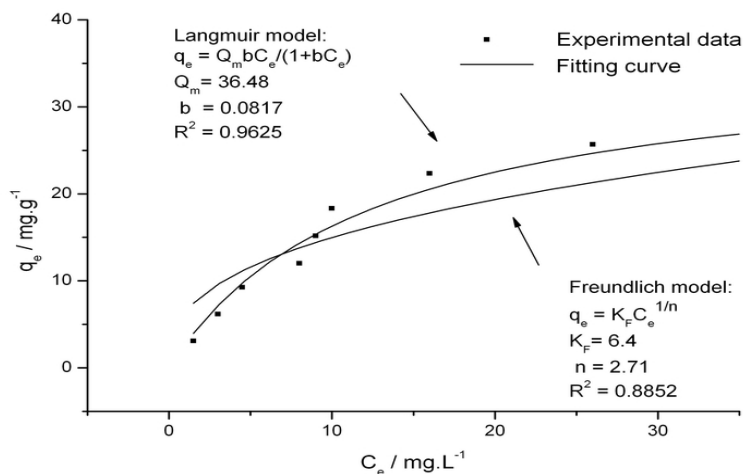


Fig. 2. Effect of initial Pb(II) concentration on the MCM-41-S9 and Langmuir, Freundlich adsorption isotherm models fitting curves.

**Effect of adsorbent dosage on adsorption.** The effect of adsorbent dosage on adsorption of Pb(II) was studied from pH of 2 to 10  $\text{g}\cdot\text{L}^{-1}$  at room temperature, constant initial Pb(II) concentration of  $20 \text{ mg}\cdot\text{L}^{-1}$ , and contact time of 2 h. Fig. 4 shown the effect of adsorbent dosage on the adsorption of Pb(II) onto MCM-41-S9. it indicated that  $C_e$  decreased with the increase of dosage of adsorbent at the beginning of adsorption stage. When the adsorption reached equilibrium,  $C_e$  changed slowly with the constant increase of dosage.  $q_e$  decreased with the increase of dosage due to lower adsorbate concentration versus higher dosage of adsorbent. In this study, the optimum dosage was 4 to 6  $\text{g}\cdot\text{L}^{-1}$  at

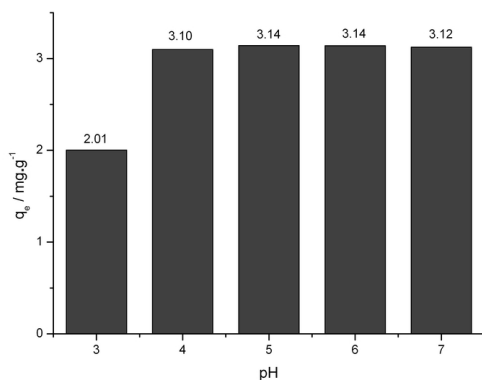


Fig. 3. Effect of initial pH of solution on the Pb(II) adsorption onto MCM-41-S9.

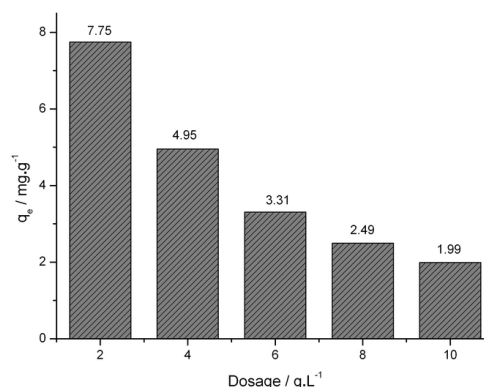


Fig. 4. Effect of adsorbent dosage on the Pb(II) adsorption onto MCM-41-S9.

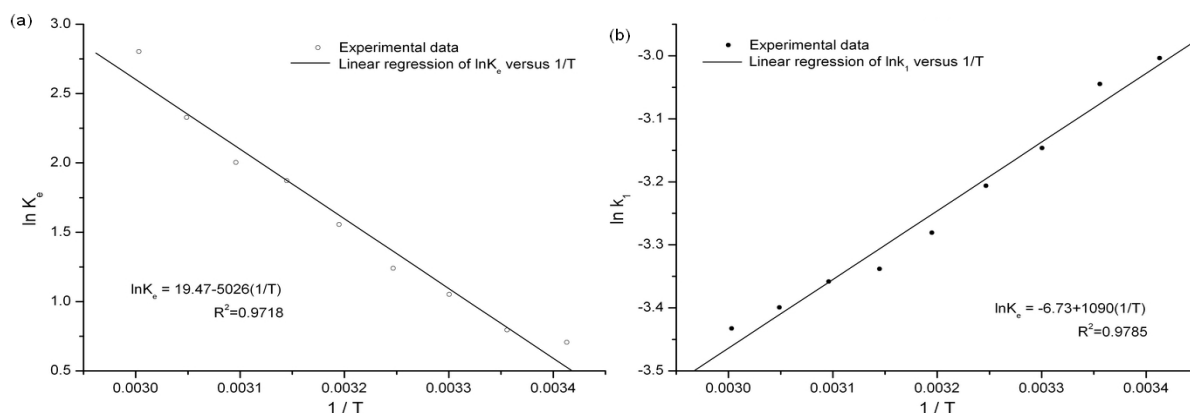


Fig. 5. Effect of temperature on the Pb(II) adsorption onto MCM-41-S9.

**Effect of temperature on lead adsorption.** The effect of temperature on adsorption of Pb(II) was studied from 293K to 333 K at constant initial Pb(II) concentration of  $20 \text{ mg}\cdot\text{L}^{-1}$ , and contact time of 2 h. Fig.5 shows the plots of  $\ln K_e$  and  $\ln k_1$  versus  $1/T$ , respectively. The adsorption thermodynamics parameters, such as  $E$ ,  $\Delta G_0$ ,  $\Delta S_0$  and  $\Delta H_0$ , were shown in Table 3. It showed that with increasing temperature, and  $K_e$ , as well as adsorption capacity of Pb(II) increased.  $K_e$  increased that it indicated more Pb(II) was removed by adsorbent. Since adsorption is an endothermic process ( $\Delta H_0 > 0$ ), it would be expected that an increase in temperature of the Pb(II)-adsorbent system would result in decreased sorption capacity.  $\Delta G_0$  was negative and decreased with an increase of temperature that meant adsorption was spontaneous and reacted in higher temperature. With an increase in temperature, the mobility of the Pb(II) increased and the retarding forces acting on the diffusing ions decreased, thereby increased the removal capacity of adsorbent.  $k_1$  decreased with an increase of temperature. The value of adsorption activation energy  $E$  was negative as showed in Table 3. It indicated that Pb(II) adsorption on MCM-41-S9 was stable and the adsorption reaction was undergoing spontaneously. It was generally known that the negative value of  $E$  indicated the adsorption reaction was exothermic. This result calculated by  $k_1$  ( $E < 0$ , exothermic) was contrary to

that ( $\Delta H_0 > 0$ ,  $\Delta G_0 < 0$ , endothermic) of  $K_e$ . the reasons for this can be explained as follows: MCM-41-S9 was not pure zeolite and contained various inorganic compositions; hence, the adsorption effect dominated the reaction which was undergoing in lower temperature. In this stage, the adsorption activation energy was negative and the reaction was stable and exothermic. With an increase of temperature, other effects such as precipitation, chemical adsorption, dominated the reaction and this might lead to the change of the reaction from the exothermic to the endothermic. This conclusion needed a further discussion on the basis of more experimental data in the future.

Table 3 Effect of temperature on  $K_e$ ,  $k_1$  and Calculation results of adsorption thermodynamics.

Adsorption equilibrium constant $K_e = q_e / C_e$									
Temperature	293K	298K	303K	308K	313K	318K	323K	328K	333K
$K_e / L \cdot g^{-1}$	2.02	2.21	2.86	3.46	4.74	6.50	7.41	10.26	16.51
Modified Pseudo-second-order kinetic model $\frac{C_t}{C_0} = 1 - \frac{m_s q_e}{C_0} \cdot \frac{q_e k_1 t}{1 + q_e k_1 t}$									
Temperature	293K	298K	303K	308K	313K	318K	323K	328K	333K
$k_1 / 10^{-2} g \cdot mg^{-1} \cdot min^{-1}$	4.96	4.76	4.30	4.05	3.76	3.55	3.48	3.34	3.23
Calculation results of adsorption thermodynamics									
$E$ / $kJ \cdot mol^{-1}$	$\Delta H^0$ / $kJ \cdot mol^{-1}$	$\Delta S^0$ / $J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G^0 / kJ \cdot mol^{-1}$						
			293K	303K	313K	323K	333K		
-9.06	96.2	338.5	-2.98	-6.37	-9.75	-13.1	-16.5		

## Summary

The optimum  $Na_2O/SiO_2$  molar ratio for the synthesis of MCM-41 type zeolites varied from 0.2 to 0.3. The formation of MCM-41 zeolite from biomass ash strongly depends on the treatment condition; high active amorphous silica was used for the synthesis of zeolite prepared by calcinations at  $800^\circ C$ . Pb(II) adsorption onto MCM-41-S9 could be described by the Langmuir isotherm model. MCM-41-S9 was adaptive and efficient to removal Pb(II) in the solutions with lower pH value; adsorption capacity increased with the increase of dosage of adsorbent at the beginning of adsorption stage; adsorption thermodynamics result have shown the reaction of Pb(II) adsorption on MCM-41-S9 was stable and undergoing spontaneously. But, by using two parameters,  $K_e$  and  $k_1$ , the reaction was evaluated to be endothermic and exothermic, respectively. This might to be explained that the reaction was dominated by different effects at initial and stable stage.

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