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Removal of Phosphorous from Aqueous Solution by Adsorption Using Laterite as Adsorbent

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ABSTRACT:Phosphates along with the nitrates, even though are the desired nutrients for plant growth within a limited quantity, when discharged in excess quantities above the prescribed limits into the water bodies causes eutrophication, which is a serious environmental problem. The undesired problems like fish kill due to depletion of dissolved oxygen as large amount of growth and decay of the plant occurs due to eutrophication. Phosphorous is discharged into water bodies from agricultural, industrial and domestic sources. Other problems caused by eutrophication are the plankton growth which causes the color of water to green or brown gives cloudy appearance to water. It diminishes the aesthetic value of water body. Adsorption is one of the most convenient methods for the removal of phosphate from water due to simplicity of its design and operation and economic feasibility.

Present work is undertaken with the objective of studying the adsorption efficiency for the removal of phosphate from its aqueous solution using laterite as a low-cost adsorbent. The batch experiments were carried out to study the influence of various operating parameters namely, pH, adsorbent dosage, contact period, and initial adsorbate concentration and also to find the best fit adsorption isotherm (Langmuir or Freundlich adsorption isotherm) by fitting the experimental data of the adsorption and to find the model constants for best fit isotherm. It was observed that under the optimal conditions the percentage removal was 91.5%.

From the results, it was found that the Freundlich equation best fits with the experimental results and the correlation coefficient (R^2) for the best fit line is 0.969, whereas for Langmuir the R^2 value is 0.935. The Freundlich constants were found to be, $n = 1.71$ and $K = 7.244$ mg/ g. Value of n greater than one indicates a good adsorption condition.

KEYWORDS:Adsorption, UV spectrophotometer, Laterite, Freundlich isotherm, Langmuir Isotherm

I. INTRODUCTION

In recent years the clean water resources are diminishing at faster rate due to increasing rate of water pollution. Increase in population, rapid growth of industrialization, mining and agricultural activities are the major causes for increase in water pollution. Hence, for the sustainable management of water resources, advanced wastewater treatment, recovery, reuse and recycling are gaining more importance for the judicious use of water resources and protecting the water bodies and water environment from the ill effects of disposal of wastewater into water bodies.

Excessive discharge of inorganic ions such as nitrates and phosphates into water bodies are the major risks for clean and natural water quality. Within a limited quantity nitrates and phosphates are desired nutrients for the growth of the plants. However, above certain quantity or concentrations, they cause eutrophication of waterbodies which is one of the undesired and serious environmental problems. Eutrophication causes fish kill due to depletion of dissolved oxygen as there will be large amount of growth and decay of aquatic plants. Ultimately it leads to ecological imbalance of organisms in the aquatic environment. Hence in recent decades there is an increasing international focus on developing the technically feasible and economic processes and techniques for the removal of these inorganic ions from the wastewater before discharging into water bodies.

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II. LITERATURE SURVEY

The reviews of some of the research papers recently published have been presented in the following paragraphs.

Loganathan et al., (2014) in their critical review on adsorption of phosphate have observed that the various types of adsorbents used for removal of phosphate are ion exchange resins, metal oxides, silicates, carbonates of magnesium and calcium, by products from industries, naturally available or manufactured chemical compounds, It is mentioned that the oxides or hydroxide of the metals like Iron, Aluminum, and highly porous polymer compounds possess large capacity for adsorption in the range of 3-115mg/gram). The capacities of adsorbents like oxides or hydroxides of iron aluminum etc. can be enhanced by pre-treatment with chemicals. In spite of having very low capacity, many wastes by products of various industries are used for adsorption of phosphorous. Such adsorbents have very low cost of manufacturing or disposing. Moreover, the limitation of low capacity may be compensated with excessive adsorbent dosages.

Stéphane et al., (2015) in their study on adsorption using apatite (natural rock phosphate) for phosphate removal from aqueous waste solution found that this process is an effective and a sustainable one. In this method, they used a particular pattern for placing the adsorbent pellets to achieve high percentage removal of phosphorous to such an extent that outlet phosphorous concentrations are less than 2.0 mg/L. Various factors and mechanisms like particle size, process kinetics, the nature of adsorbent have been reported in their paper. Also reported in the paper are the results of column studies and the operating data of industrial scale treatment plants.

Ahmed et al., (2012) carried out a study on the phosphorous adsorption by using red mud by modifying its characteristics. Their study included the effect of initial thermal treatment or activation of raw red mud on the performance efficiency of adsorption. Experiments were conducted to know the effect of various operating variables like time, temperature, adsorbent dosage etc. In this work, it is reported that the Langmuir model best fits with experimental data than the Freundlich model. Double precipitation and calcination of raw red mud were proved to be very effective activation methods. It was also reported in this work that the results of this study can also be applied to the treatment of phosphorous contaminated effluents from industries like fertilizers, phosphoric acid etc.

NING Ping, et al., (2008) carried out a study on phosphate adsorption by using zeolite adsorbents. In this work a novel adsorbent called as La(III)-modified zeolite adsorbent (LZA) was prepared. Zeolite of size 90 nanometer was prepared with another element lanthanide so as to remove the phosphate preferentially. The study was carried out along with chlorides, sulfates etc. The optimum values of various parameters as revealed by the study are as follows. Concentration of Lanthanum chloride as 0.05 mole per liter, solid liquid ratio 1:25, pH of solution 10.0, activation temperature of 550 °C for 1 one hour. It was observed that the experimental results fitted well to Freundlich isotherm model and the model constants were found to be 16.8 mg per liter for K value and the inverse of slope as 0.221. The distribution constant was 36.6 at 6 pH and regeneration of the adsorbent was carried out to the extent of almost 100% with sodium chloride solution. It was concluded that the adsorbent used in the study is significantly effective for adsorption of phosphate from the domestic waste.

C.R.Ramakrishnaiah, and Vismitha (2012) in their research work on the phosphorous removal by adsorption, used different types of low cost adsorbent materials. The adsorbents used the sludge obtained from alum water treatment, the ash obtained from burning of coal, and the blast furnace slag and fly ash from the thermal power plant. For the sludge fly ash, and the slag, the optimum values for pH and dosage were 5.0 and 100 g/L respectively. However, for the ash obtained by burning of the coal, the optimum values were observed to be 7 and 75 g/L. For continuous operation (column experiments), the time of equilibrium (saturated condition) was obtained by plotting a breakthrough graph.

III. THEORY OF ADSORPTION

The process of adsorption is surface phenomenon wherein the solute (adsorbate) present in the solution transfer on surface layers of solid substance called adsorbent present into the liquid phase by physical and chemical process. In the waste water treatment adsorbate is the pollutant present in the waste water and the adsorbent is a solid material with a porous structure. By using adsorption process, different types of pollutants like phosphate, fluoride, heavy metals, color causing substances etc. can be removed effectively and economically. The design and operation

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of the process is also very simple compared to other physic-chemical processes like absorption, stream stripping, chemical and biological degradations etc. Another significant advantage of adsorption process is that the adsorbent can be easily regenerated by using a suitable desorption process.

The materials used as adsorbents in the adsorption process may be taken from different origins. They may be mainly categorized into 1) The Natural materials 2) the wastes generated or the byproduct from Industrial, Agricultural and Domestic sources like bagasse, fly ash, red mud etc. and 3) Synthesized materials (Organic or Inorganic). Adsorbent may be in the form of rods, spherical pellets or monolithic. The hydrodynamic diameter ranges from 0.5 to 10 mm size. Thermal stability of adsorbents should be as high as possible. Pores of small diameters results in larger exposed surface area. Other important parameters of adsorbents are porosity, density, selectivity specific surface area, adsorption capacity and catalytic properties. The most important property of an adsorbent is the specific surface area which is measured in m^2/g adsorbent.

The cost of adsorbent is major factor that has a significant influence on the economic feasibility of the adsorption process. Keeping this in mind, a naturally occurring low cost material, laterite is taken as adsorbent in the present work.

Types of adsorption isotherms: Freundlich, Langmuir and BET (Brunauer, Emmet and Teller) are the most commonly used equations that are used to describe experimental isotherm data. Freundlich isotherm is empirical equation whereas the Langmuir isotherm has a rational theoretical basis.

Freundlich Isotherm: Basically, Freundlich isotherms is empirical in nature. But later it was interpreted that it has heterogeneous surfaces supporting the theory of sites of variable affinities. According to this theory, the stronger bonding sites occur first and then it increases with decrease in degree of site occupation.

The general form of Freundlich equation is,

$$q_e = K C_e^{1/n}$$

Where,

q = mass of adsorbate/mass of adsorbent

K = freundlich constant with respect to quantity or capacity of removal (mg/g)

C_e = Concentration of adsorbate in solution at Equilibrium n = constant

The Parameters for Freundlich Isotherm can be determined by rearranging the above equation in a linear form as follows.

$$\ln q_e = \ln K + (1/n) \ln C_e$$

The plot of $\ln q_e$ Vs $\ln C_e$ will be a straight line having slope equal to $1/n$ and with intercept of $\ln K$.

However, this isotherm has a drawback that it works properly at lower pressure and fails at higher pressure.

Langmuir Isotherm: This equation which is a semi empirical one was first developed by Irving Langmuir in 1918. This is applicable gases or fluids adsorbed on solid adsorbents. It is derived based on statistical thermodynamics and works better at high temperature and pressure. Important assumptions made in deriving this equation are

- Molecules adsorbed at equilibrium will be equal to the number of molecules desorbed from the adsorbed site. Thus, it is considered as a dynamic process and the adsorbed layer is considered to be one molecule thick.
- Equivalent number of adsorption sites.
- Only one molecule is accommodated by each site.
- Energetically homogeneous Surface and no interaction between adsorbed molecules.
- No phase transitions.
- Adsorption occurs on localized sites on the surface. At optimum adsorption, a single layer is formed..

The Langmuir equation is expressed as

$$q = q_m \cdot b \cdot C_e / (1 + b \cdot C_e)$$

Where,

q_e = ratio of mass of solute adsorbed to the mass of adsorbent (mg/g.)

C_e = Concentration of adsorbate in solution at equilibrium (mg/L).

q_m and b = Constants that represent capacity and energy of adsorption respectively.

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IV. METHODOLOGY

The present study was carried out using the batch adsorption experiments at room temperature. The solution of predetermined concentration was taken in beaker containing the required dosage of adsorbent. The solution containing the adsorbent was kept under continuous stirring for a required length of contact time. Then the solution was filtered to get clear solution free from adsorbent. The clear solution was analyzed for determining the concentration of phosphorous remained in the solution. Initially the batch experiments were conducted at a given initial concentration of phosphorous, adsorbent dosage and the contact time for different values of pH to determine the pH corresponding to the maximum removal of phosphorous. Further tests were conducted at this optimum pH to find the influence of initial concentration of P, contact time and the dosage. From the analysis of the results obtained, the optimum values of initial concentration of P, dosage and time of contact were determined. By using these optimum parameters, experiments were carried out to get the values of Freundlich and Langmuir constants by plotting the graph of best fit straight line. The percentage removal of phosphorous from solution was calculated by using equation below:

$$\text{Percentage Removal} = \frac{C_0 - C_i}{C_0} \times 100\%$$

Where

C_0 is the initial concentration of phosphorous

C_i is final concentration of phosphorous.

V. RESULTS AND DISCUSSION

Figure 1: Initial concentration of P, dosage, and contact period constant at 10.0 mg/L, 2 g and 60 minutes respectively. The surface charge and ionization degree gets affected significantly during adsorption process by the variation in pH. In the present work, in order to determine pH at which the maximum percentage removal occurs, experiments were carried out at various values of pH from 2 to 10 keeping the other parameters of initial concentration of P, dosage, and contact period constant at 10.0 mg/L, 2 g, and 60 minutes respectively.

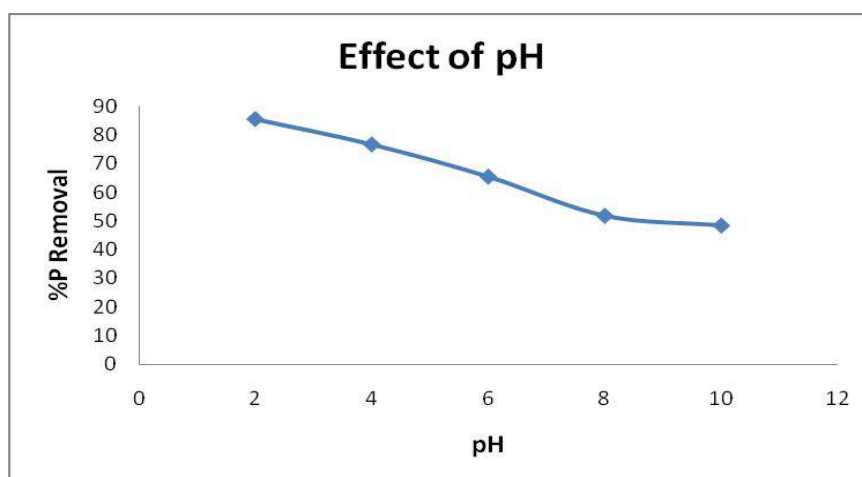


Figure 1. Effect of pH

Figure 2: In this case batch experiments were conducted to study the influence of adsorbent dosage. The dosage was varied from 0.5 to 2.5 grams by keeping the other parameters namely, pH, initial concentration, contact time constant at 2, 10 g/L, and 60 minutes respectively. The experimental results are graphically represented. From the Figure it can be observed that the percentage removal increases initially up to the adsorbent dosage of 2.0 grams and then decreases

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with a further increase in the dosage. Therefore it can be inferred that the maximum percentage removal of 91.8% of phosphorous occurs at an adsorbent dosage of 2.0 grams.

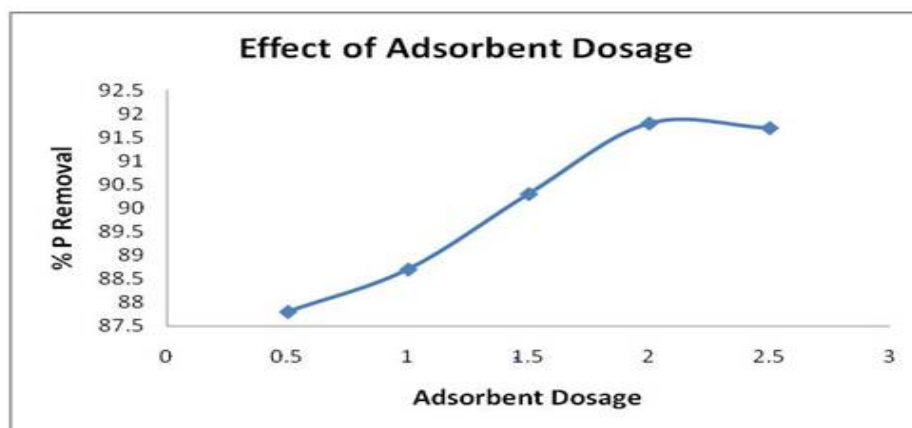


Figure 2. Effect of adsorbent dosage

Figure 3: Contact time affects the adsorption process significantly. Experiments were conducted out to determine the optimum contact time by varying the contact period in the range of 30 to 150 minutes by keeping the other parameters namely, pH, dosage and starting concentration constant at 2, 1.5 grams, and 10 mg/L respectively. From the results it is observed that the contact period for the maximum removal 120 minutes.

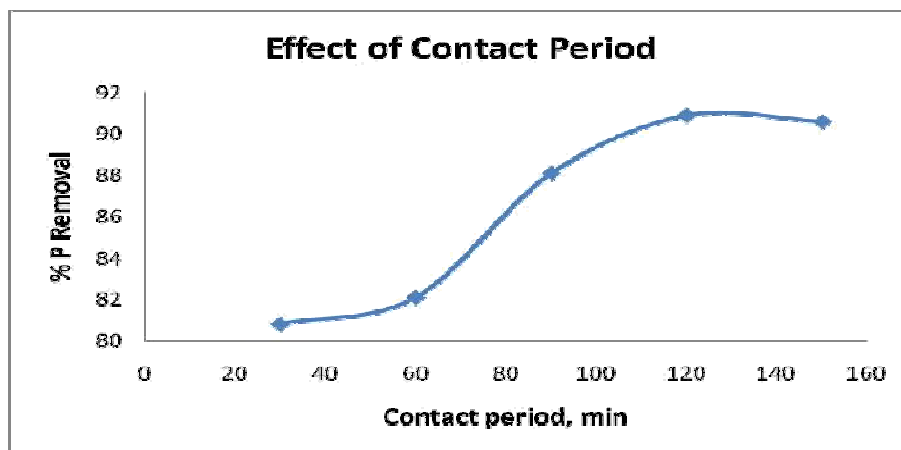


Figure 3. Effect of contact period

Figure 4: Experiments were carried out to study the effect of initial concentration of phosphorous in the solution. Phosphorous concentration was varied in the range of 10 to 50 mg/L while keeping the other parameters namely, pH, adsorbent dosage, and contact time constant at 2, 1.5 mg/L, and 120 minutes respectively. The results are shown graphically in Figure 4. From the graph, it can be observed that, the percentage removal increased gradually for first three concentrations and with further increase in concentration it almost reached equilibrium as there was not much change in the percentage removal. This observation can be explained by the fact that as the phosphorous/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites. This results in decrease in the adsorption efficiency. Hence, the optimum initial phosphorous concentration in present study is taken as 40mg/L.

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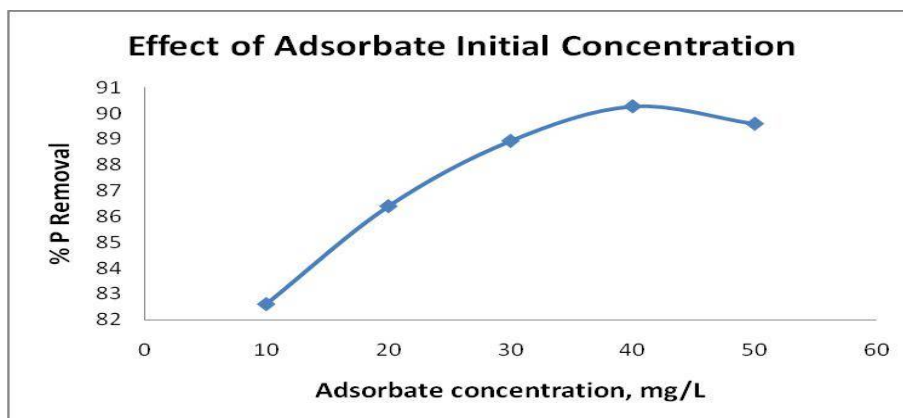


Figure 4. Effect of contact period

Figure 5: From the below Figure, the values of slope and the intercept are 0.033 and 0.112 respectively. The Langmuir constants q_m and b related to capacity and energy of adsorption respectively, can be determined from the values of slope and intercept as follows.

Slope = $1/q_m = 0.033$ Hence $q_m = 1/0.033 = 30.3$

Intercept = $1/(q_m \times b) = 0.112$ Therefore $b = 1/(30.3 \times 0.112) = 0.29$

The correlation coefficient for best fit straight line $R^2 = 0.935$

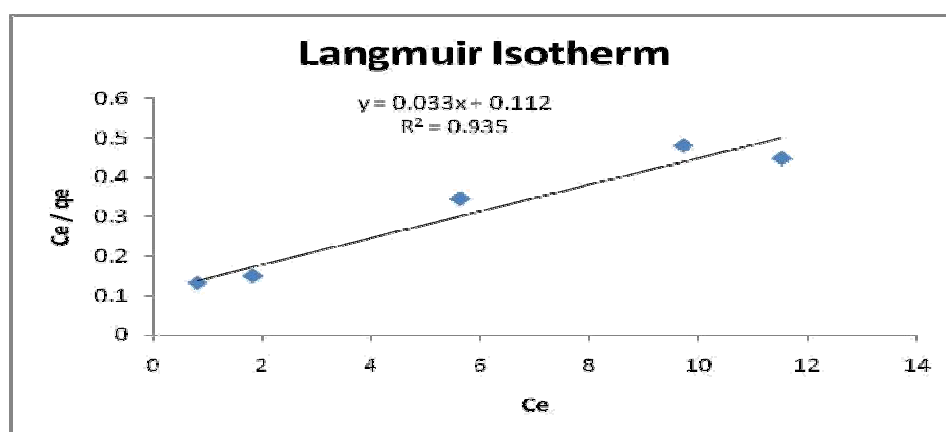


Figure 5. Langmuir isotherm for phosphorus adsorption on laterite.

Figure 6: From the graph it is observed that the slope of the best fit line is 0.584 and intercept is equal to 0.860. Hence the Freundlich constant $n = 1/0.584 = 1.71$ and constant K which represents the adsorption capacity is equal to $10^{0.86} = 7.244$ mg/g. Correlation coefficient for the best fit line $R^2 = 0.969$

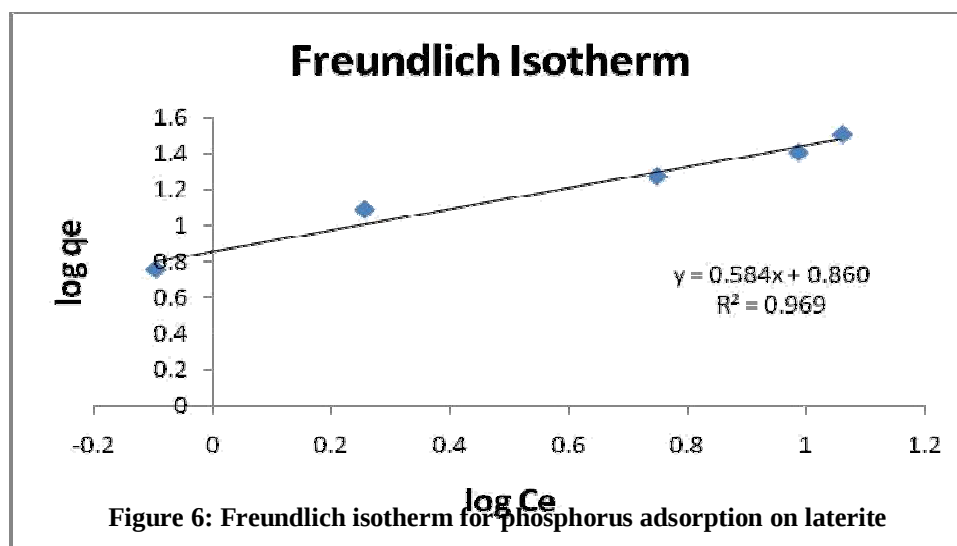
Since the n value is greater than 1, it can be said that the adsorption is a favorable process. From the above results it can be seen that, the Freundlich equation holds better than the Langmuir equation for the adsorption of phosphate from its aqueous solution since the experimental data best fits the model.

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VI. CONCLUSION

The present work was carried to study the removal of phosphate from the synthetic solution using laterite as adsorbent. The results indicate that the laterite can be effectively used for the phosphate removal by adsorption from aqueous solution of Di Ammonium Phosphate.

Various operating parameters namely the pH, dosage of adsorbent, contact period and initial adsorbate concentration were optimized by carrying out the experiments in appropriate ranges. From the results, it was found that the optimum values for pH, dosage of adsorbent, contact period and initial adsorbate concentration were 2, 2.0 mg/L, 120 minutes and 40 mg/L respectively. Under these conditions the percentage removal of phosphate was 91.5%.

Two adsorption isotherms namely, the Langmuir and the Freundlich isotherms were tested for fitting the experimental results. From the results, it was found that the Freundlich equation best fits with the experimental results and the correlation coefficient (R^2) for the best fit line is 0.969, whereas for Langmuir the R^2 value is 0.935.

The Freundlich constants were found to be, $n = 1.71$ and $K = 7.244$ mg/ g. The n value greater than 1 indicates a good adsorption condition.

Overall it is concluded that the laterite which is available abundantly and at a comparatively lesser cost, can be effectively applied as a suitable adsorbent for the removal of phosphorous from the aqueous solution.

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