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Adsorption of caprolactam from aqueous solution by novel polysulfone microcapsules containing [Bmim][PF_6]

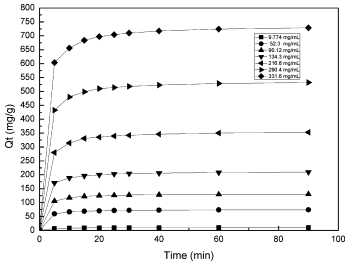
Dong-xuan Chen[a], Xiao-kun OuYang[a,b], Yang-guang Wang[b], Li-ye Yang[b], Ke-jun Wu[a], Chao-hong He[a,*]

[a] State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027 PR China
[b] School of Food and Pharmacy, Zhejiang Ocean University, Zhoushan 316004 PR China

HIGHLIGHTS

- Ionic liquid [BMIM][PF_6] has been encapsulated in polysulfone.
- The microcapsules containing ionic liquid have been used for the first time to extract caprolactam from water.
- The adsorption kinetics and sorption isotherm have also been discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Polysulfone (PSF) microcapsules containing ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) as extractant have been successfully prepared using solvent evaporation method and used in removing caprolactam from water. The results showed that ionic liquid [Bmim][PF_6] was successfully encapsulated by PSF and the encapsulation capacity of 32.44% was achieved. Systematic studies on the effect of concentration of ammonium sulfate solution, caprolactam adsorption equilibrium, kinetic and isotherm by PSF@[Bmim][PF_6] capsules were carried out. The results showed that increasing the concentration of ammonium sulfate solution, initial concentration of the caprolactam and the adsorption time were good for adsorption. The adsorption kinetics of caprolactam followed pseudo-second-order model and the Freundlich equation described the adsorption process better than the Langmuir equation. These PSF@[Bmim][PF_6] capsules showed potential ability in the treatment of wastewater.

1. Introduction

During the production process of caprolactam, which is the monomer of nylon 6, a large quantity of wastewater is discharged. In the wastewater, there is a low concentration of caprolactam [1]. The ingestion of such contaminated water into the human body can cause convulsion and also damage the spleen and the central nervous system [2]. Conventional method for the removal of caprolactam is solvent extraction. Benzene is the most widely used extractant [1,3–5], and toluene[6], ethers [7] and esters [7] as new solvents instead of benzene are also used in caprolactam recovery. Because of the negative effects on health and environment of these solvents, a new environmentally benign solvent has to be chosen to remove caprolactam in replacing of traditional toxic solvent.

Ionic liquids have advantages including practically no vapor pressure, nonvolatile at environment temperature, high conductivity, as well as easy-tuned physical and chemical properties by varying the component ions [8]. Ionic liquids have already been used in the removal of aromatic hydrocarbons [9], and amino acids

* Corresponding author. Tel.: +86 571 87952709; fax: +86 0571 87951742.
E-mail addresses: xkouyang@163.com (X.-k. OuYang), chhezju@zju.edu.cn (C.-h. He).

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[10,11]. In our previous work, we also used ionic liquids to recover caprolactam from water and found ionic liquids had higher distribution ratios than benzene and toluene [12].

Although ionic liquid has many advantages on pollutants extraction, it also has a shortcoming that stands in its way of being used in industry. The shortcoming is that ionic liquid has high viscosity, which could influence the mass and heat transport during extraction. Immobilizing ionic liquids in microcapsules is a way to overcome this disadvantage. Using microcapsules in separation can minimize the use of organic solvent and make phase separation easily. Nowadays microcapsules have been successfully used in metal recovery [13,14]. Kazuo [15] even made a column in which microcapsules containing organic solvent were packed. This column was used to separate gallium and indium. However, the examples of using microcapsules containing ionic liquid to separate pollutants are little, nearly none.

In this work, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) were encapsulated in polysulfone (PSF) using solvent evaporation method and this new microcapsules were used in caprolactam separation. The characteristics of the microcapsules have been characterized. The effect of ammonium sulfate concentration and the adsorption performance of the microcapsules were also investigated.

2. Materials and methods

2.1. Chemical reagents

Ionic liquid [Bmim][PF_6] (>99 wt%) was obtained from Lanzhou Greenchem ILS, LICP. The shell material PSF (intrinsic viscosity: 0.59) was supplied by Shupeng Plastic Co., Ltd. Dichloromethane (DCM, >99.5 wt%) was bought from Sinopharm Chemical Reagent Co., Ltd. Gelatin (>99 wt%) was purchased from Tianjin Damao Co. Caprolactam (>99 wt%) was obtained from J&K chemical Co., Ltd. Ammonium sulfate (>99 wt%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Throughout the study, deionized water was used. All chemicals were used as received without any further purification.

2.2. Preparation of microcapsules containing extractant

Samples of 6 g [Bmim][PF_6] and 2 g PSF were mixed with 25 mL DCM. Then the mixture was added to 200 mL of gelatin solution (0.8 wt%) with magnetic stirring at 400 rpm. After DCM evaporated completely, the PSF microcapsules containing [Bmim][PF_6] were obtained. The prepared microcapsules were collected by filtration, washed with deionized water several times and finally dried. The morphology of microcapsules was characterized by means of a polarizing microscope (ECLIPSE E600POL, NIKON, Japan). The encapsulation capacity of [Bmim][PF_6] was measured by thermogravimetric analyzer (TGA, Pyris 1, Perkin-Elmer, American) at temperature range of 25–800 °C with 20 °C/min heating ramp in nitrogen atmosphere.

2.3. Adsorption experiments

The adsorption experiment was carried out using a batch reactor to a temperature controlled water bath. An amount of 8 g extractant microcapsules were added into 80 mL of caprolactam solution, and then the mixture was shaken together. The adsorption amounted of caprolactam was calculated by the difference between its initial and final concentrations. According to the results we got earlier [12] and the composition of the real waste water [3], different adsorption operating conditions, such as concentration of ammonium sulfate solution (0–0.3 g/mL), contact time (5–90 min), initial caprolactam concentration (10–300 mg/mL) and temperature (30, 50 and 70 °C), were taken into account.

Caprolactam concentration in the solution was determined by a high performance liquid chromatography (HPLC). The chromatographic system consisted of a Waters 600CONTROLLER system and a UV detector. The mobile phase was 35% methanol in water and the flow-rate was 1 mL/min. The detection wavelength was 240 nm, and the separation temperature was 30 °C. The injection amount was 5 μL.

The amount of caprolactam adsorbed Q_t, was calculated according to the following equation:

$$Q_t = (C_0 - C_t)\frac{V}{W} \quad (1)$$

where C_0 and C_t are the initial concentration and concentration at different time of caprolactam solution (mg/mL), respectively, Q_t is adsorption capacity of caprolactam per unit capsules at different time (mg/g), V is the volume of the caprolactam solution (mL) and W is the mass of the extractant microcapsules used (g).

3. Results and discussion

3.1. Characterization of extractant microcapsules

3.1.1. Diameter and morphological observation

Fig. 1 shows polarizing microscope images of the microcapsules. The microcapsules are essentially monodisperse and spherical in shape. The average diameter is 44.2 μm.

3.1.2. Thermogravimetric analysis

TGA was used to quantify the encapsulated amount of [Bmim][PF_6] in the microcapsule. The TGA graph is shown in

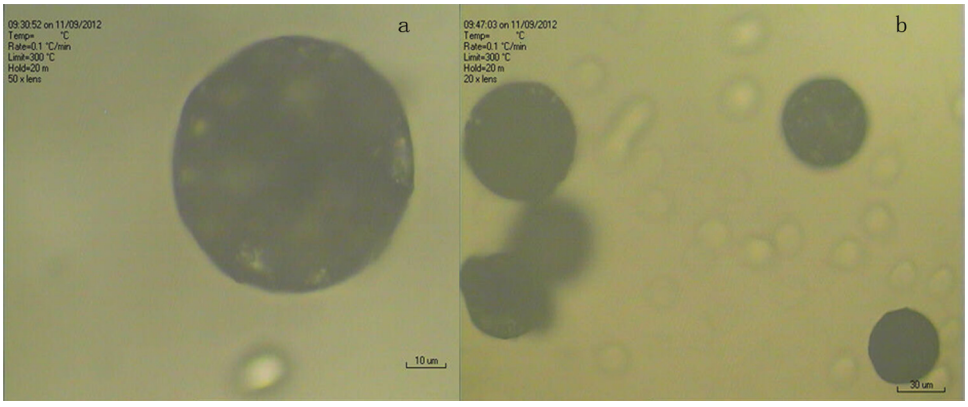

Fig. 1. Polarizing microscope image of PSF@ [Bmim][PF_6]: (a) 50× lens;(b) 20× lens.

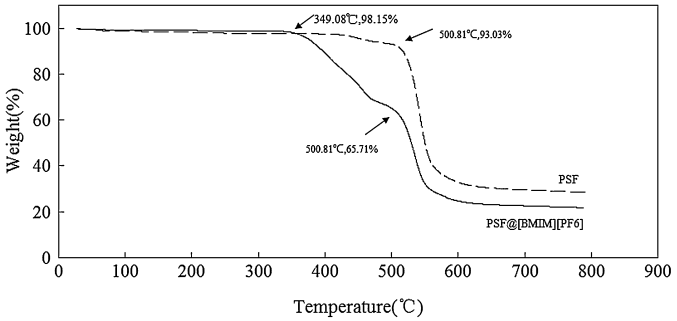

Fig. 2. TGA of the microcapsules.

Fig. 2. The weight loss (32.44%) at a temperature range of 349.08–500.81 °C can be assumed to be the decomposition of [Bmim][PF_6], while PSF started to decompose at 500.81 °C. The result agrees with several previous literature [16–18]. The encapsulation capacity of the microcapsules as calculated is 32.44%, which is better than the earlier report [17]. The TGA results also show that the microcapsules are stable under 300 °C, which means the microcapsules can be used below 300 °C. But during the preparation process, some ionic liquid was not encapsulated. That might be due to that some ionic liquid formed an independent phase in water and did not be encapsulated in microcapsules.

3.2. Adsorption studies

3.2.1. The contribution of [BMIM][PF_6] and PSF for caprolactam

The PSF@[BMIM][PF_6] capsules include PSF and [BMIM][PF_6]. In order to investigate the adsorption contribution of [BMIM][PF_6], PSF and PSF@[BMIM][PF_6] capsules, they were used to remove caprolactam, respectively. 2.59 g (the encapsulation amount of [BMIM][PF_6] in 8 g PSF@[BMIM][PF_6] capsules) of [BMIM][PF_6], 5.41 g (the content of PSF in 8 g PSF@[BMIM][PF_6] capsules) of PSF capsules and 8 g of PSF@[BMIM][PF_6] capsules were added into 80 mL 9.77 mg/mL caprolactam solution, respectively. Since the preparation process is a physical process, the extraction character of ionic liquid in the microcapsules equals that of free ionic liquid. Also the ionic liquid inside the microcapsules have enough space to form an ionic liquid phase which is the same as the free ionic liquid. And using microcapsules is easier for phase separation. As is well known, liquid–liquid extraction has a rapid adsorption rate. So, it is not surprised to see that [BMIM][PF_6] presents a faster adsorption rate than PSF@[BMIM][PF_6] capsules from Fig. 3. Although the adsorption equilibrium time is a little longer when using PSF@[BMIM][PF_6] capsules than using [BMIM][PF_6], it has a little better adsorption ability when using PSF@[BMIM][PF_6] capsules because of the little adsorption contribution by PSF. Also it is easier for phase separation when using PSF@[BMIM][PF_6] capsules.

3.2.2. Effect of concentration of ammonium sulfate solution

The effect of ammonium sulfate on the adsorption of caprolactam is shown in Fig. 4. It can be seen that with the presence of ammonium sulfate, the amount of adsorption increases with the increase of the concentration of ammonium sulfate. The ammonium sulfate may increase the interaction between caprolactam and ionic liquid in the microcapsules [12]. So, the presence of ammonium sulfate could enhance the adsorption process.

3.2.3. Effect of initial caprolactam concentration and contact time

The effect of initial caprolactam concentration and contact time on adsorption efficiency is summarized in Fig. 5. It is found that the initial adsorption rate of caprolactam is fast and most of caprolactam have been adsorbed within the first few minutes. Then,

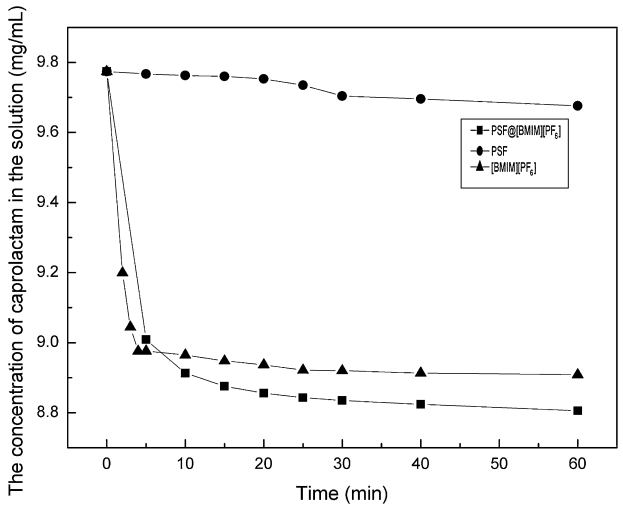

Fig. 3. Adsorption of caprolactam by PSF@[BMIM][PF_6] capsules, [BMIM][PF_6], and PSF capsules (C_0: 9.77 mg/mL, 30 °C).

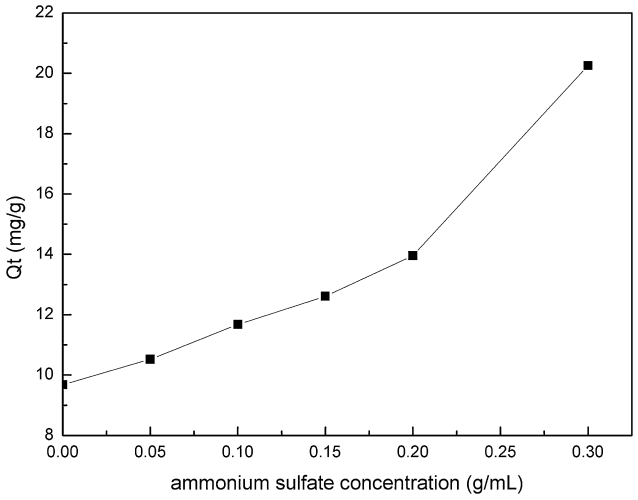

Fig. 4. Effect of concentration of ammonium sulfate solution (C_0: 9.77 mg/mL, 30 °C, shaking time = 2 h).

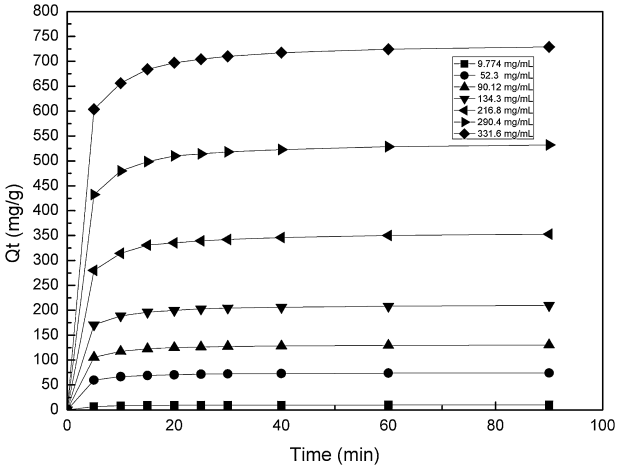

Fig. 5. Effect of initial caprolactam concentration and contact time on the adsorption caprolactam amount from aqueous solutions (30 °C).

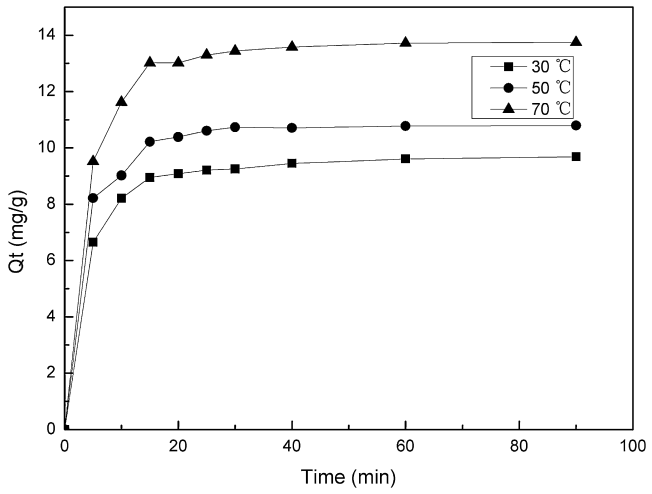

Fig. 6. Effect of temperature on the adsorption caprolactam amount from aqueous solutions (C_0: 9.77 mg/mL).

the adsorption rate slows down with the passing of time. The amount of adsorption increases by the time elapsed and equilibrium is achieved within 60 min. Moreover, the initial rate of adsorption is greater for higher initial caprolactam concentration. The amount of caprolactam adsorbed at equilibrium per gram of capsules increases with the increase of the initial concentration over the range tested.

3.2.4. Effect of temperature

The effect of temperature on the caprolactam adsorption was studied with the constant initial caprolactam concentration of 9.77 mg/mL in the range of 30–70 °C. Fig. 6 shows the effect of temperature on the capraolactam adsorption as a function of shaking time. As can be seen in Fig. 6, the temperature increase results in the adsorption rate increase when the temperature of adsorption experiment increased from 30 to 70 °C. Also, the equilibrium adsorption capacity increases with the temperature rising. This indicates that the adsorption process is endothermic, so higher temperature is more effective for the adsorption of caprolactam.

According to Fig. 6, the thermodynamic parameters standard free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) can be calculated by the following equations [19]:

$$\Delta G^0 = -RT \ln K_0 \tag{2}$$

$$\ln K_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{3}$$

where K_0 ($=Q_e/C_e$) is equilibrium constant. Q_e represents equilibrium adsorption capacity of caprolactam on capsules (mg/g) and C_e stands for equilibrium concentration of caprolactam solution (mg/mL). These thermodynamic parameters are presented in Table 1. The negative ΔG^0 values verify that the adsorption process can spontaneously happen. Positive value of ΔH^0 confirms the adsorption process is endothermic, which is consistent with the conclusion we got above. The positive value of ΔS^0 indicates that there is an increase in the randomness in the system.

Table 1
Thermodynamic properties for the caprolactam sorption.

Temperature (K)	K_0	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ/mol)	ΔS^0 (J mol/K)
303	1.10	−0.240	10.8	35.9
323	1.24	−0.581		
343	1.82	−1.71		

3.3. Adsorption modeling

3.3.1. Adsorption kinetics of caprolactam

Adsorption rate data are analyzed using the pseudo-first-order kinetic model and pseudo-second-order equation, respectively, by applying the following equation [14,18,20,21]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{4}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where Q_t is the amount of caprolactam adsorbed per unit mass of capsule (mg/g) at various time t, Q_e stands for the maximum adsorption capacity (mg/g), k_1 represents the pseudo-first-order rate constant for the adsorption process (min^{-1}), and k_2 is the pseudo-second-order rate constant for the adsorption (g/mg/min). The resultant parameters are given in Table 2. The pseudo-second-order model gives a better representation of the data than the pseudo-first-order model. This shows the pseudo-second-order model does satisfy the kinetics of caprolactam adsorption.

3.3.2. Adsorption isotherm of caprolactam

The Langmuir adsorption isotherm model and Freundlich adsorption isotherm model are the most popular models in investigating the character of the adsorption process. The well known expressions of the Langmuir and Freundlich equations in linear forms can be represented as follows [22,23]:

$$\text{Langmuir equation} \frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}} \tag{6}$$

$$\text{Freundlich equation} \ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where C_e (mg/mL) is the concentration of the caprolactam solution at equilibrium and Q_e (mg/g) represents the amount of adsorption at equilibrium. In the Langmuir equation, $Q_{\max}$ is the maximum adsorption capacity and K_L stands for the Langmuir constant. In the Freundlich equation, K_f and $1/n$ are empirical constants. The values of the isotherm constants are presented in Table 3. From the results,

Table 2
The adsorption kinetic model rate constants for caprolactam on capsules at.

C_0 (mg/mL)	Q_e[a] (mg/g)	Pseudo-first-order			Pseudo-second-order		
		Q_e[b] (mg/g)	k_1 (min^{-1})	R_1^2	Q_e[b] (mg/g)	k_2 (g/mg/min)	R_2^2
9.77	9.69	3.52	0.0546	0.771	9.92	0.0501	0.998
52.3	74.1	21.2	0.0543	0.724	75.2	0.0101	0.995
90.1	130	34.4	0.0547	0.687	132	0.00639	0.999
134	210	56.7	0.0543	0.702	212	0.00381	0.993
217	353	100	0.0525	0.699	358	0.00206	0.991
290	532	142	0.0536	0.691	541	0.00151	0.992
332	729	192	0.0543	0.699	741	0.00113	0.999

[a] Experimental.
[b] Calculated.

Table 3
The Langmuir and Freundlich equations, the related parameters and correlation coefficients (30 °C).

Langmuir			Freundlich		
Q_{max} (mg/g)	K_L (mL/mg)	R^2	K_f (mg/g) (mL/mg)$^{1/n}$	n	R^2
629	0.00205	0.728	0.653	0.812	0.995

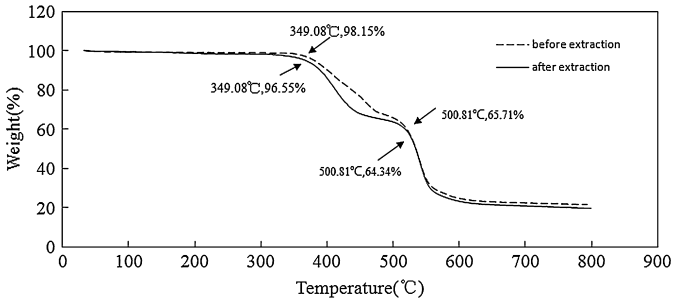

Fig. 7. TGA of microcapsules before and after different initial caprolactam concentrations (30 °C) extraction.

it can be seen that the best fit is found with the Freundlich model with an R^2 value of 0.995. It can be assumed that the adsorption process is reversible and occurs on heterogeneous sites with non uniform distribution of energy levels [22].

3.4. Stability of microcapsules

To use the microcapsules on an industrial scale, it is necessary to make sure that they are stable after extraction. So, the TGA method was employed to investigate the ionic liquid capacity in microcapsules after extraction. As can be seen from Fig. 7, the encapsulation capacity became 32.21% from 32.44%. The loss of ionic liquid is small and could be neglect during industrial process. This indicates that using microcapsules containing [Bmim][PF_6] to recovery caprolactam from water, is possible for potential industrial applications.

4. Conclusion

Polysulfone microcapsules containing [Bmim][PF_6] have been prepared successfully and these microcapsules are used to adsorb caprolactam from aqueous solution. The characterization studies by using polarizing microscope and TGA proves that [Bmim][PF_6] was successfully encapsulated into the PSF microcapsules, and the encapsulation ratio achieved 32.44%. The adsorption equilibrium time was less than 50 min under different experiment conditions and it obeyed the pseudo-second-order kinetic model. The Freundlich model could describe the adsorption process well. The results reported in this work could be important in wastewater treatment.

Acknowledgments

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