

Adsorption of hexavalent chromium onto organic bentonite modified by the use of iron(III) chloride

Jianchao Hao, Leilei Xiao, Huifen Liu, Lijun Shi, Xiaoyan Xu, Bin Lian and Congqiang Liu

ABSTRACT

The adsorption of hexavalent chromium (Cr(VI)) was improved by using organic bentonite (OB) modified with iron(III) chloride. The adsorption mechanisms and characteristics of OB and organic bentonite modified by FeCl₃ (FMOB) were studied by using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and energy dispersive X-ray spectroscopy (EDS). It was found that hydroxyl-iron replaced some of the calcium and magnesium contained in the FMOB, but no significant change in its structure was shown even though the adsorption experiments proved that FMOB had a better Cr(VI) adsorption ability compared to OB. The coated material was prepared by mixing FMOB and 4A molecular sieves in a coated pot for the adsorption experiments in the test column. The relevant results showed that the adsorption of the coated material retained its high adsorption ability and maintained that ability after desorption and regeneration, which implied a potential for further application.

Key words | adsorption, coated materials, hexavalent chromium, modification, organic bentonite

Jianchao Hao

Leilei Xiao

Bin Lian (corresponding author)

Jiangsu Key Laboratory for Microbes and Functional Genomics,

Jiangsu Engineering and Technology Research Centre for Microbiology,

College of Life Sciences, Nanjing Normal University, Nanjing 210023,

China

E-mail: bin2368@vip.163.com

Jianchao Hao

Huifen Liu

Lijun Shi

Xiaoyan Xu

College of Agronomy and Resources and Environment,

Tianjin Engineering Research Center of Agricultural and Environment Remediation,

Tianjin Agricultural University, Tianjin 300384, China

Congqiang Liu

State Key Laboratory of Environmental Geochemistry,

Institute of Geochemistry,

Chinese Academy of Science, Guiyang 550002, China

INTRODUCTION

Chromium is widely used in areas as diverse as electroplating, alloying (e.g. in stainless steel), leather tanning, and in pigment and textile dyes (Asgari *et al.* 2008; Akar *et al.* 2009; Giri & Patel 2011). Chromium exists in two stable oxidation states, Cr(III) and Cr(VI), the latter being a known human carcinogen (Panda *et al.* 2011). Drinking water polluted by Cr(VI) can cause cancer, and exposure to Cr(VI) by inhalation has already been declared as carcinogenic (Haney *et al.* 2012; Sharma *et al.* 2012; Tziritis *et al.* 2012). Also, Cr(VI) can induce energy metabolism disturbances (Xiao *et al.* 2012) and it is therefore important to treat wastewater containing Cr(VI) to a high standard.

The advantages of using natural clays as adsorbents are that they are inexpensive, environmentally friendly, and offer good adsorption and ion exchange capabilities (Sarkar *et al.* 2010), but natural clays such as bentonite are negatively charged and show no affinity for Cr(VI) (Krishana *et al.* 2009; Li *et al.* 2009). Some cationic surfactants are reported as being

used to modify bentonite to improve its adsorption of Cr(VI) (Mansri *et al.* 2009; Brum *et al.* 2010; Hu & Luo 2010; Guerra *et al.* 2013). In addition, montmorillonite-supported magnetite nanoparticles (Yuan *et al.* 2009) and bentonite-supported nanoscale zero-valent iron (Shi *et al.* 2011) also showed good adsorption of Cr(VI), which showed Fe or its chemical compounds may help bentonite to adsorb Cr(VI). The present preliminary experimental work also showed that a combination of organic bentonite (OB, a by-product produced from octadecyl trimethyl ammonium chloride (OTAC)) and FeCl₃ (a cheap reactant) could improve the Cr(VI) adsorption by OB. There have been few reports concerning the adsorption of Cr(VI) by organic bentonite modified by FeCl₃ (FMOB). The adsorption mechanisms of FMOB are an important topic to study in a deeper way.

In this paper, the adsorption of Cr(VI) with FMOB and its adsorption mechanisms were studied to develop a new way to treat Cr(VI) contamination. The paper also provides

theoretical and practical bases for controlling Cr(VI) contamination in practice.

MATERIALS AND METHODS

Materials

FMOB preparation

OB (a milk-white powder, graded through a 300 mesh sieve) was produced by Tianjin Shuangrui Co. Ltd. The surfactant contained in the OB was OTAC. OB (250 g) and deionised water (500 mL) were thoroughly mixed in a 1 L beaker and then 50 g/L of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was added until the pH of solution was approximately 6. The mixture was stirred using a magnetic stirrer for 40 min. Then, the solution was filtered using quantitative filter paper. The solid collected on the filter paper was dried, ground (grinder model PCS0808, China), and then screened through 120 mesh sieves to yield the FMOB.

OB and FMOB were analysed by X-ray diffraction (XRD, D/Max-2200, Rigaku, Japan) (Yao *et al.* 2013) and Fourier transform infrared spectroscopy (FTIR, Nexus-670, USA) (Sarkar *et al.* 2010); their morphology and composition were observed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS, JSM-5610LV, Japan) (Lu *et al.* 2012).

Preparation of coated materials

Spherical 4A molecular sieves (200 g) were added to a coated pot and heated until the temperature reached approximately 50 °C. Then, an ethanol solution of rosin glyceride (20%) was sprayed into the coated pot, FMOB was added and mixed, and then the coated FMOB was formed. After that the coated material was heated to evaporate the solvent (Wang *et al.* 2006); finally, the coated FMOB was soaked in a 5% hydrochloric acid solution for 1 h for activation, and then filtered and dried.

Adsorption experiments

Cr(VI) adsorption capacity of OB and FMOB

Aqueous Cr(VI) solution (50 mL, 20 mg/L) was added to 100 mL conical flasks, then adsorbent (0.20 g) was added to each conical flask (three replicates). The mixtures were maintained at temperature of 30 °C and shaken in an

end-over-end shaker at 140 rpm for 40 min (the same conditions were used in subsequent experiments). Then, the solutions were filtered using quantitative filter paper and the Cr(VI) concentration in the filtrate was analysed by atomic absorption spectrophotometry (AAS, TAS-986, China). The removal of Cr(VI) was calculated using the expression

$$\theta = \frac{(c_0 - c_s)}{c_0} \times 100$$

θ : removal efficiency (%)

c_0 : initial Cr(VI) concentration (mg/L)

c_s : Cr(VI) concentration after treatment (mg/L).

The residue on the filter paper was observed by SEM-EDS to determine the surface morphology and chemical composition respectively.

Variation in Cr(VI) removal with different adsorbent dosage

Aqueous Cr(VI) solution (50 mL, 20 mg/L) was added to 500 mL flasks and 0.1, 0.2, 0.4, 0.6, and 0.8 g of FMOB were added to them, respectively. The solutions were filtered and the filtrate used for Cr(VI) analysis by AAS.

Variation in Cr(VI) removal with pH

Aqueous Cr(VI) solution (50 mL, 20 mg/L) was added to 12 100 mL flasks. Aqueous hydrochloric acid and potassium hydroxide were used to adjust the pH of each solution (to 1.44, 2.21, 3.17, 4.35, 5.12, 6.01, 6.88, 7.48, 9.47, 10.03, 10.84, and 12.68). Then, FMOB (0.1 g) was added to each flask. The solution was then filtered and the filtrate used for Cr(VI) analysis by AAS. The distribution of Cr(VI) compounds in an aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ solution (20 mg/L) could be calculated using Visual MINTEQ software at different pH levels.

Cr(VI) adsorption capacity analysed by adsorption isotherm

Aqueous Cr(VI) solutions (50 mL) having different concentrations (5, 10, 20, 30, 40, and 50 mg/L) were added to 100 mL flasks and FMOB (0.1 g) was added to each. The solutions were filtered and the filtrates used for Cr(VI) analysis by AAS. The amount adsorbed was calculated as follows:

$$q_e = \frac{(c_0 - c_e) \times 50 \times 10^{-3}}{0.1}$$

q_e : amount adsorbed (mg/g)
 c_0 : initial Cr(VI) concentration (mg/L)
 c_e : equilibrium concentration of Cr(VI) (mg/L).

Adsorption/desorption of Cr(VI) onto coated material in the adsorption column

The adsorption system consisted of two parts: a metering pump, and an adsorption column (13.80 mm in diameter, 250 mm in length). Cr(VI) solution (20 mg/L) was passed through the adsorption column from top to bottom and the Cr(VI) concentration of the collected effluent was determined by AAS at different times.

A 0.1 mol/L potassium hydrate solution was used as a desorption agent after adsorption and 0.5 mol/L hydrochloric acid was used as the regeneration agent: regeneration was conducted until the pH value of the effluent reached a value of between 2 and 3.

RESULTS AND DISCUSSION

Adsorption experiments

Cr(VI) adsorption by OB and FMOB

The Cr(VI) removals of OB and FMOB were $52.7 \pm 0.02\%$ and $97.2 \pm 0.55\%$ respectively, which showed that OB can adsorb Cr(VI), but its adsorption capacity was lower than that of FMOB. FMOB could significantly increase the adsorption of Cr(VI) and it was therefore used as an adsorbent in subsequent experiments.

Variation in Cr(VI) removal with FMOB dosage

When the dosage was 0.1 g, the Cr(VI) removal efficiency from an aqueous solution (50 mL, 20 mg/L) was $87.46 \pm 1.54\%$. Doubling the dosage to 0.2 g increased the removal efficiency to more than $98.95 \pm 0.12\%$, but higher dosages did not produce a significantly different result. Therefore, the dosage was set to 2 g of adsorbent in 1 L of Cr(VI) solution (20 mg/L) in subsequent experiments.

The variation in Cr(VI) removal of FMOB with pH

The change in Cr(VI) removal efficiency with pH is shown in Figure 1.

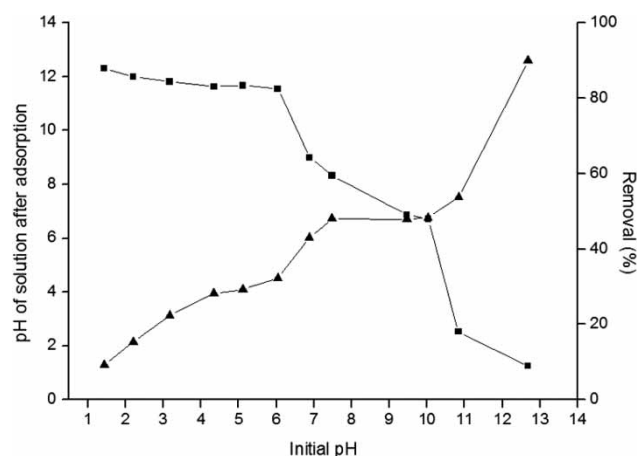


Figure 1 | Cr(VI) removal of FMOB with pH (pH after adsorption (▲) and removal (■)).

The pH value of the solution was an important controlling parameter in the adsorption process. The removal efficiency was examined at different pH values (1.44, 2.21, 3.17, 4.35, 5.12, 6.01, 6.88, 7.48, 9.47, 10.03, 10.84, and 12.68) and the results showed no significant change when the initial pH value was increased from 1.44 to 6.01, suggesting that increasingly more acidic conditions only had a small influence on Cr(VI) removal, and the maximum adsorption was obtained at the initial pH of 1.44 (Figure 1). In contrast, Cr(VI) removal decreased rapidly when the initial pH was increased from 6.88 to 12.68; it may have been that the combination between OH^- and cationic groups (OTAC and hydroxyl-iron) on bentonite prevented Cr(VI) adsorption. The pH of the Cr(VI) solution after adsorption was smaller than the initial pH (Figure 1). The decrease in pH of the solution after adsorption may have been related to the hydroxyl-iron on the FMOB.

Cr(VI) adsorption capacity analysed by adsorption isotherm

The data obtained from adsorption isotherms were analysed by the Langmuir model. The Langmuir isotherm obtained using OB had the form: $c_e/q_e = 0.1525c_e + 1.5356$ ($R^2 = 0.9927$) and that from FMOB had the form: $c_e/q_e = 0.0904c_e + 0.1322$ ($R^2 = 0.9644$). Their adsorption capacities were 6.56 and 11.06 mg/g respectively. Thus, the adsorption capacity of FMOB was much greater than that of OB. The results for the adsorption capacity of FMOB were similar to those for the modified bentonite using the surfactant Arquad 2HT-75 (Sarkar *et al.* 2010) and modified montmorillonite with hydroxylaluminum and cetyltrimethylammonium bromide (Hu & Luo 2010). However,

commercially available OB was cheaper (at market price) and its modification with FeCl_3 was easier. Therefore, FMOB showed potential with regard to its application in the removal of Cr(VI) from wastewater in practice.

Characterisation of FMOB and the adsorption mechanism

The use of analytical tools – XRD, FTIR, SEM, and EDS – allowed the recognition and identification of the formation mechanisms of the interchange of hydroxyl-iron and chromium with the ions (Ca and Mg) present in the bentonite.

XRD patterns obtained from OB and FMOB are shown in Figure 2.

There was no significant difference in the wave pattern between OB and FMOB according to Figure 2, which showed that modification of OB with FeCl_3 did not change the basic structure of the OB.

FTIR analysis (Figure 3) also produced a similar result to those found by XRD (Figure 2): there were no significant differences in the wave pattern between OB and FMOB in Figure 3, lines (a) and (b).

SEM images showed the surface morphology of OB (Figure 4(a)), FMOB (Figure 4(b)) and FMOB after Cr(VI) adsorption (Figure 4(c)): it was difficult to recognise any significant differences between them. The EDS data showed that the chemical compositions had changed (Figures 4(a) and 4(b)): the Ca and Mg content decreased and the Fe content increased (Figure 4(b)), which meant that the composition of the OB changed when it was modified by the FeCl_3 . The SEM images showed that Cr(VI) adsorption by FMOB caused no significant change to the surface morphology of the FMOB.

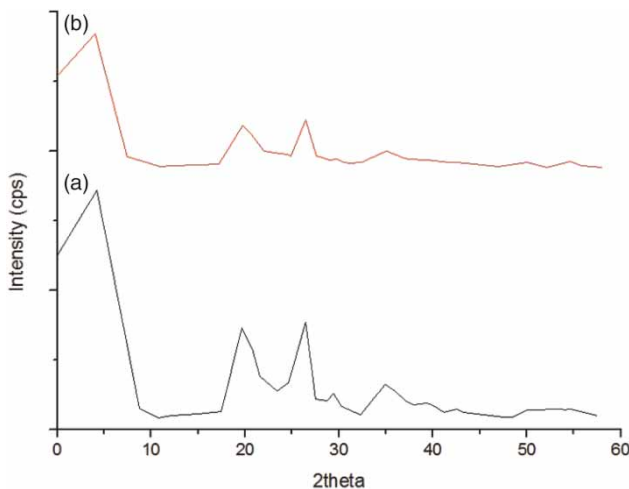


Figure 2 | XRD patterns: OB (a) and FMOB (b).

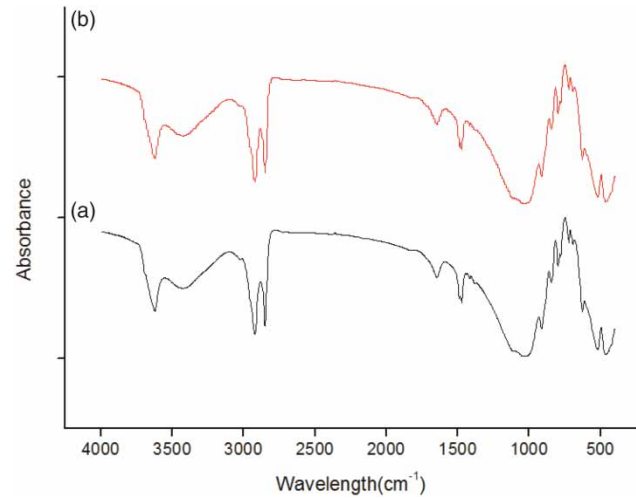
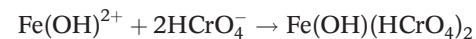
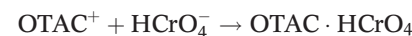


Figure 3 | FTIR spectra of OB (a) and FMOB (b).

The appearance of Cr peaks in the EDS confirmed the Cr(VI) adsorption by the FMOB (Figure 4(c)).

The decreased Ca and Mg contents in the FMOB may have a relationship with ion exchange: Fe^{3+} was transformed into hydroxyl-iron for hydrolysis and the hydroxyl-iron constituent mainly contained $\text{Fe}(\text{OH})^{2+}$ (>99%) when the pH of the solution (1 to 500 mg/L Fe^{3+}) was 6 according to MINTEQ software calculations. Hydroxyl-iron, which was positively charged, could replace Ca and Mg in the FMOB (Figure 4(b)), which may have led to an increase in the Cr(VI) adsorption capacity.

The results calculated using Visual MINTEQ software at different pH levels showed that the concentration of HCrO_4^- decreased with an increase in pH whereas the concentration of CrO_4^{2-} increased. The Cr(VI) removal efficiency was greater than 82.5% when the pH value was below 6.01 and the removal efficiency decreased rapidly when the pH increased beyond 6.01 (Figure 1). This phenomenon showed that HCrO_4^- combined with the adsorbent more readily than CrO_4^{2-} . The reason for this was that HCrO_4^- might have combined with OTAC and $\text{Fe}(\text{OH})^{2+}$ more easily in this reaction system. The main adsorption mechanism might have entailed the following chemical reactions:



Adsorption of Cr(VI) onto coated FMOB in the column

Coated FMOB was filled in the column to decrease pressure loss of adsorption in the column. The data of

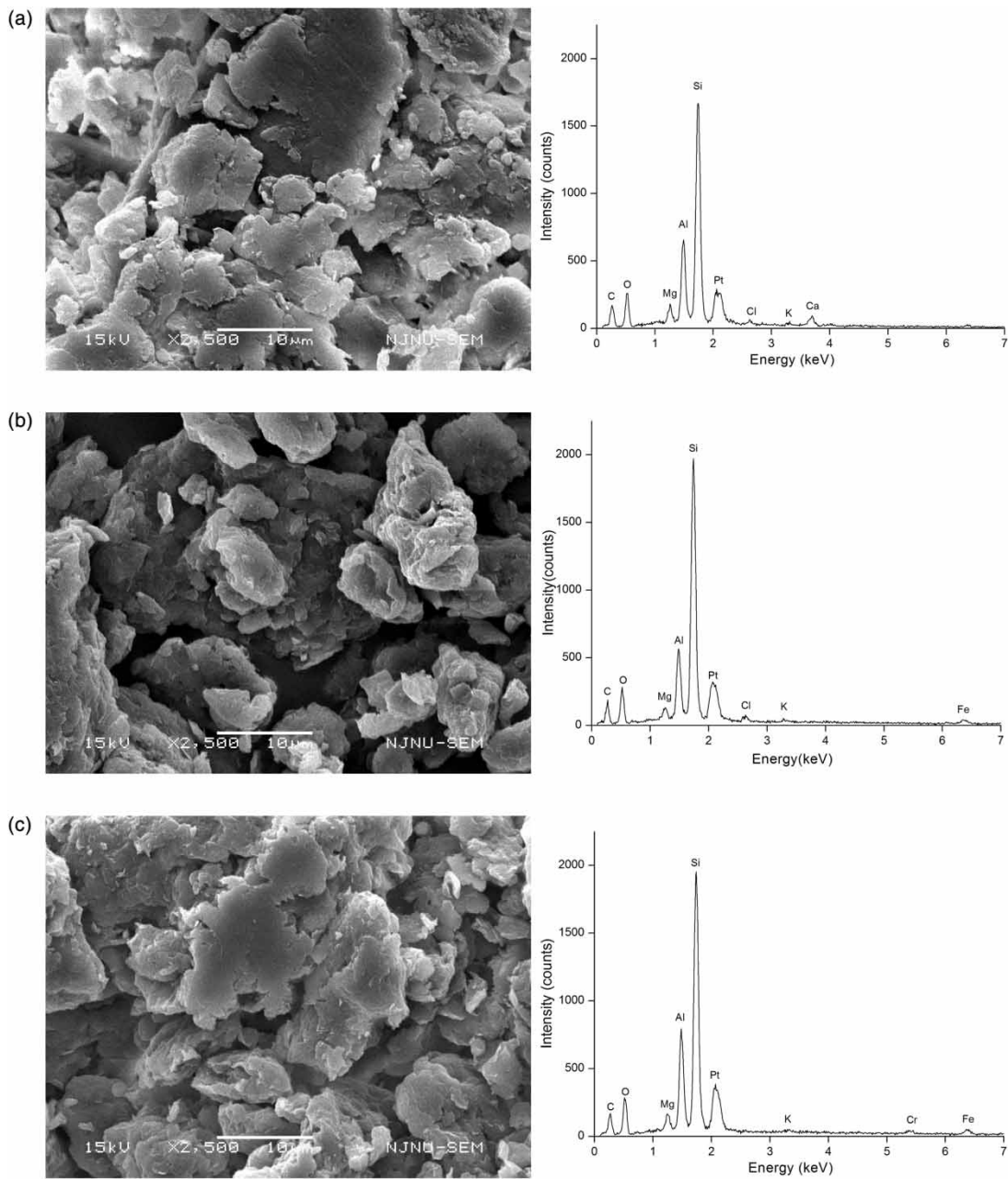


Figure 4 | SEM images and EDS results: OB (a), FMOB (b) and FMOB after Cr(VI) adsorption (c).

Cr(VI) concentration in the effluent were fitted to a modified Thomas model (Tabakci & Yilmaz 2008) described as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th}q_e x}{v} - K_{Th}C_0 \ln t$$

C_t : Cr(VI) concentration of effluent at a certain time (mg/L)

C_0 : Cr(VI) concentration of stock solution (mg/L)

K_{Th} : mass transfer rate constant (10^{-3} L/[ln(min)·mg])

q_e : equilibrium absorption capacity (mg/g)

x : mass of absorbent (g)

v : flow rate (mL/min)

t : time (min).

In this modified Thomas model, $\ln t$ was substituted for t in the original Thomas model; the meaning of K_{Th} , q_e , v , and x were the same as in the original Thomas model. Obviously $\ln(C_0/C_t - 1)$ presents a linear relationship to $\ln t$. The linear equations of the first, second, and third adsorptions were described as follows:

$$\ln(C_0/C_t - 1) = -0.8769 \ln t + 3.4555 \quad (R^2 = 0.9779)$$

$$\ln(C_0/C_t - 1) = -0.8675 \ln t + 4.3522 \quad (R^2 = 0.9855)$$

$$\ln(C_0/C_t - 1) = -0.9371 \ln t + 4.0914 \quad (R^2 = 0.9562)$$

q_e can be calculated by linear equation; q_e for the first, second, and third adsorptions was 2.26, 2.51, and 2.88 mg/g respectively and q_e increased with increased adsorption time, which proved that the adsorption capacity of the coated FMOB did not decrease after desorption–regeneration.

CONCLUSIONS

1. FMOB had a better adsorption capacity than OB, and the maximum adsorption capacity was found to be 11.06 mg/g; so the optimum dose of FMOB was 2 g in 1 L Cr(VI) solution (20 mg/L).
2. Cr(VI) removal decreased slightly when the pH value increased from 1.44 to 6.01 and the optimum pH was approximately 6 when the quality of the effluent was considered.
3. The modification mechanism involved hydroxyl-iron replacing some of the Ca and Mg contained in the OB. Hydroxyl-iron greatly improved the Cr(VI) adsorption onto the FMOB.
4. The adsorption in the column followed a modified Thomas model. The coated materials were easily desorbed and regenerated and also retained their high adsorption capacity after desorption and regeneration.

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