

RESEARCH ARTICLE

## Optimization of parameters for effective removal of Cr(VI) species by burnt brick clay

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**Abstract:** The extent of removal of Cr(VI) species from aqueous solution by brick particles is highly dependent on the firing temperature of brick clay used for removal of Cr(VI) species, since many physical and chemical changes occur during firing. The highest removal of Cr(VI) species by brick clay is obtained with clay fired at 200 °C. The amount of suspended matter is low with brick clay fired at temperatures ranging from 200 °C to 600 °C as seen with turbidity measurements. Optimization of parameters, such as duration of stirring (10 minutes) and settling time period (2 hours), leads to 60% removal of Cr(VI) by brick particles fired at 200 °C in batch experiments, without pH control, despite the negative charge of the source of Cr(VI). Dynamic experiments conducted in packed columns also effectively remove Cr(VI). The extent of removal does not significantly depend on solution pH up to 11 and on common interferents.

**Keywords:** Burnt brick clay, chromium, optimization, turbidity.

### INTRODUCTION

Chromium occurs naturally as compounds with Cr(III), and is mined as  $\text{FeCr}_2\text{O}_4$ <sup>1</sup>. The health hazards associated with exposure to chromium depend on its oxidation state. Hexavalent chromium [Cr(VI)] is a highly water soluble carcinogen, which causes respiratory problems, and damage to eye and throat. The reduced form [Cr(III)] is less soluble and less toxic<sup>2,3</sup>. Cr(VI) is used in many industrial processes such as metal finishing, leather manufacturing and synthetic dye production<sup>4</sup>. It is therefore present in industrial waste waters in larger amounts as compared to Cr(III). This results in interaction of Cr(VI) with natural systems, such as soil or clay.

The extent of interaction of a metal ion with mineral surfaces depends on many factors such as solution

pH, surface acidity, pre-treatment, contact time and temperature of interaction<sup>5-7</sup>. Such interactions are also controlled by the presence of other ions, organic matter and microbes which would form thin films on mineral surfaces<sup>3,8</sup>. Findings from small-scale laboratory investigations of the effect of experimental variables on these interactions can be used to develop methodologies for removal of heavy metals from aqueous systems using solid adsorbents.

In addition to direct adsorption, another approach to detoxify Cr(VI) in water is reduction by bacteria-generated reducible species such as sulfide or ferrous ions<sup>9</sup>. Surface catalyzed chemical reduction of Cr(VI) by metal oxides and low molecular weight organic substances have also been reported<sup>10,11</sup>. Further, many clay minerals, including kaolinite, montmorillonite,  $\text{TiO}_2$  and  $\text{SiO}_2$ , are found to inhibit the sulfide reduction of Cr(VI) to various degrees<sup>12</sup>. This reaction is activated by elemental sulfur that is formed during the oxidation of sulfide. In these cases, susceptibility of Cr(III) to oxidation is a concern if all chromium species are not completely and irreversibly removed by the system employed.

It has been shown that the equilibrium concentration of Cr(VI) in soil systems containing low molecular weight organic acids such as oxalic and tartaric acids is significantly affected by pH, suggesting that the toxicity of Cr(VI) in soil environments is a complex issue<sup>13</sup>. The chemical reduction of Cr(VI) by sulfides in aqueous kaolinite suspensions was found to be of second order with respect to  $\text{H}^+$ , while it is of first order with respect to Cr(VI), the major reactant, demonstrating the active involvement of  $\text{H}^+$  for Cr(VI) – kaolinite interactions<sup>12</sup>. The above observations and other reports on interactions

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of Cr(VI) with different substrates demonstrate the complexity of this heterogeneous system<sup>14-16</sup>. The different effects shown by these substrates cannot be explained only by their differences in specific surface area alone.

Minerals undergo many chemical and physical changes on heat treatment owing to many irreversible reactions, including removal of residual water and oxidation of metal centers<sup>17</sup>. If adequate temperature and other experimental conditions are satisfied, phase changes may also occur<sup>18</sup>. Therefore, the temperature at which treatment is performed is another variable to be considered when the affinity of a metal ion towards an adsorbent is considered.

As brick particles are a poorly characterized heterogeneous material, microscopic information of brick-metal ion interactions is not completely understood. However, sorption and ion exchange properties of brick particles towards certain ionic species have recently been reported<sup>19,20</sup>. Nevertheless, chemical investigation of the brick particle - Cr(VI) system has not been widely addressed.

The objective of this research study is to investigate the ability of heat-treated brick clay to remove Cr(VI) from aqueous medium. Optimization of the removal process is performed by changing experimental parameters, such as duration of stirring, settling time period, solution pH and temperature of firing of brick clay in batch experiments, and monitoring turbidity of the resulting solutions. The results are then extended for treatment of larger volumes under dynamic conditions. Synthetic Cr(VI) solutions with the addition of interferents commonly found in industrial effluents are also used to investigate the possibility of extension of this methodology to real situations.

## METHODS AND MATERIALS

*Materials:* Standard solutions of Cr(VI) were prepared using analytical grade  $K_2Cr_2O_7$  (BDH Chemicals, USA). Solutions of different pH were prepared using NaOH and HCl. Raw clay used to make bricks (brick clay) was obtained from a kiln in Peradeniya. Raw brick clay samples fired in the laboratory at different temperatures up to 900 °C were used for all experiments. Fired brick clay samples were separated into appropriate sizes using a set of sieves. All batch experiments were conducted with brick particles of diameter ( $d$ ) < 1.0 mm, while columns used for dynamic experiments were packed with larger particles of average dimension of 0.5 cm.  $KNO_3$ ,  $Na_2SO_4$  and  $CuCl_2$  were used to investigate interference effects on Cr(VI) removal.

*Instrumentation:* A Carbolite CTF 12/100/900 furnace was used to fire brick clay samples. Turbidity of each solution was measured using a turbidity meter (HF Scientific Inc., USA, Model DRT15CE), while a Spectro-Electronic M Series atomic absorption spectrophotometer (AAS) was used to measure the total Cr concentration of all solutions. Suspensions obtained when aqueous Cr(VI) solutions were treated with brick particles [brick particle - Cr(VI) suspensions] were filtered under suction to obtain the supernatant solution free of suspended particles before AAS measurements. X-ray fluorescence studies were conducted using the X-ray fluorescence spectrophotometer (Fischerscope Model-DF500FG-456).

*Research Design:* Brick clay being a natural substance having a variable composition, poses many difficulties in quantitative analysis. Consequently, the method of sampling and the number of trials selected had to be given sufficient attention. Representative samples were thus prepared by grinding many pieces of raw brick clay samples randomly obtained, followed by firing at predetermined temperatures. The firing process was conducted by scanning the temperature from the ambient value up to the desired firing value at a rate of approximately 10 °C min<sup>-1</sup>, and allowing the firing temperature to be constant for 4 h. This was followed by cooling due to natural convection. The extent of removal of Cr(VI) by brick particles in each experiment was determined as a percentage using the following relationship.

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100 \quad \dots (1)$$

where  $C_i$  is the initial concentration of Cr(VI), which is 20 ppm unless otherwise stated, and  $C_f$  is the total concentration of Cr present in the supernatant solution of brick particle - Cr(VI) suspensions.

In order to investigate equilibrium properties, samples (10 g) of brick clay fired at 400 °C were shaken with 100 cm<sup>3</sup> of the Cr(VI) solution and allowed to settle. The total Cr concentration in the supernatant solution was then measured to determine the extent of removal. The above procedure was repeated for different periods of stirring (0, 5, 10, 15, 20, 25 and 30 min) and settling time periods (0, 30, 60, 90, 120, 150, 180 and 240 min), keeping either the period of stirring or settling time period constant. After optimization of the period of settling and the stirring time period for brick clay fired at 400 °C, the firing temperature was optimized by determining the extent of removal of Cr(VI) after treatment of Cr(VI) solutions with brick particles fired at selected

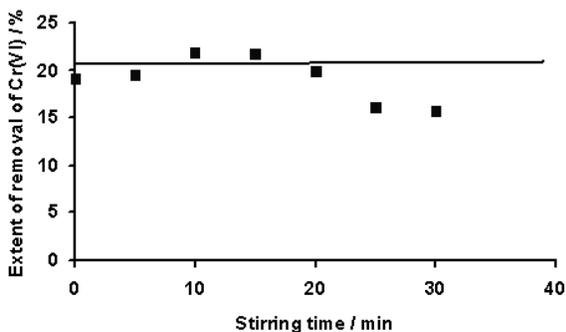
temperatures from 100 °C to 900 °C. Additionally, turbidity of the supernatant solution, obtained after treatment of Cr(VI) solution with brick particles, was monitored under different firing temperatures of brick (and a constant settling time period) as well as at different periods of settling (with brick fired at 200 °C).

The following experiments were then performed under the conditions optimized for different periods of stirring, settling time periods and firing temperatures of brick clay. The effect of pH on Cr(VI) removal was investigated by determining the extent of removal at different levels of solution pH from 1 to 14 maintained using the NaOH/HCl system. The effect of ionic strength on Cr(VI) removal was investigated by treatment of brick particles with Cr(VI) solutions of different ionic strengths prepared in KNO<sub>3</sub> solutions of concentration varying from 0.001 mol dm<sup>-3</sup> to 1.0 mol dm<sup>-3</sup>. Cr(VI) solutions (20.0 ppm) were then prepared with one interferent at a time of the same concentration, and treated with brick particles to investigate the influence of the ions commonly present in industrial effluents on Cr(VI) removal.

Experiments under dynamic conditions were performed by packing a glass column of diameter 3.5 cm up to a height of 10 cm with brick particles fired at 200 °C. The Cr(VI) solution was then passed in 100 cm<sup>3</sup> aliquots through the packed column until there was no further removal of Cr.

## RESULTS AND DISCUSSION

The extent of removal of Cr(VI) with brick clay particles fired at 400 °C in batch experiments (under static conditions) is 20% as determined using Equation (1), which provides accurate values as the brick matrix does not contain any detectable chromium according to X-ray fluorescence investigation. This temperature was specially selected as it was the optimum firing

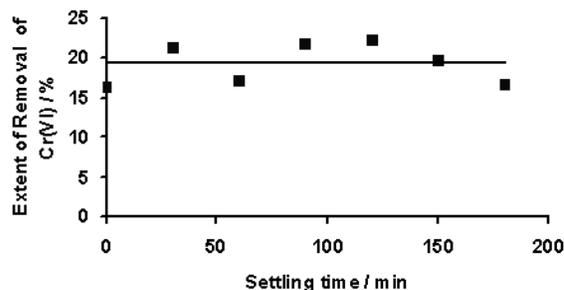


**Figure 1:** Extent of removal of Cr(VI) by fired brick particles at different stirring times for 2 h settling time ( $d < 1$  mm, 10 g brick clay fired at 400 °C, 100.0 cm<sup>3</sup> solution).

temperature for the removal of Cr(III) (Priyantha N. and Seneviratne C., unpublished results). It was further found that there was no significant change in the equilibrium concentration of total chromium in the aqueous phase even if brick particle-Cr(VI) suspensions were stirred for up to 30 minutes followed by a 2 hour settling time period (Figure 1). The slight decrease after 15 minutes stirring time may be due to the equilibrium nature of the Cr(VI) adsorption process. Further, the percentage removal, determined for different time periods of settling up to 3 hours, shows no significant difference (Figure 2). These observations clearly indicate that the heterogeneous brick-Cr(VI) solid/liquid two-phase system achieves the equilibrium within a short period of time. It can be therefore recommended that 10 minutes of stirring time and 2 hours of settling time lead to adequate removal of Cr(VI) from solution by brick clay fired at 400 °C. These optimum values are comparable with the removal of Cr(III) by brick particles (Priyantha N. and Seneviratne C., unpublished results).

Establishment of equilibrium within a short period of time is probably due to the exposure of surface adsorption sites as a result of firing. Owing to this fact, evaluation of properties of the Cr(VI)/brick system at equilibrium, such as adsorption coefficients and the extent of removal, would lead to reliable interpretation to achieve meaningful conclusions. It should however be noted that the extent of removal of Cr(VI) species is less compared to that of Cr(III) as reported elsewhere<sup>21</sup>. Burnt brick clay with a negative charge shows weaker adsorption of negatively charged ions. This is also supported by earlier reports that raw brick clay bears a negative charge above pH of 6<sup>20</sup>.

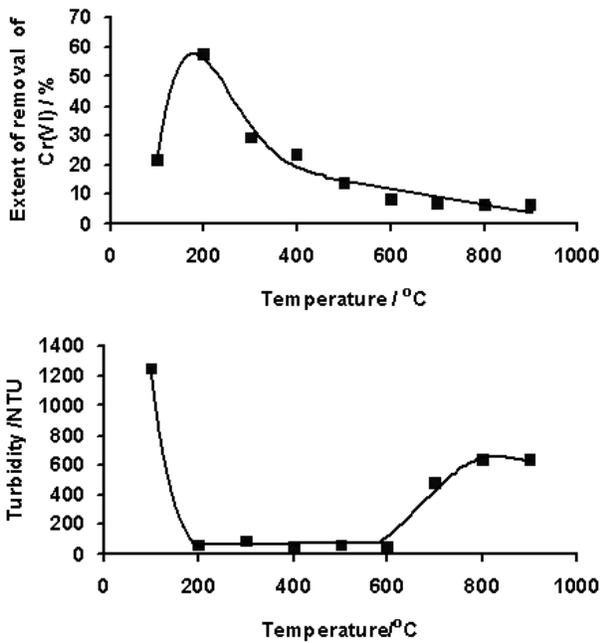
Figure 3 shows the effect of firing temperature of brick clay on the extent of removal of Cr(VI). The variation shown in the figure does not have any obvious trend, probably due to complex physical and chemical



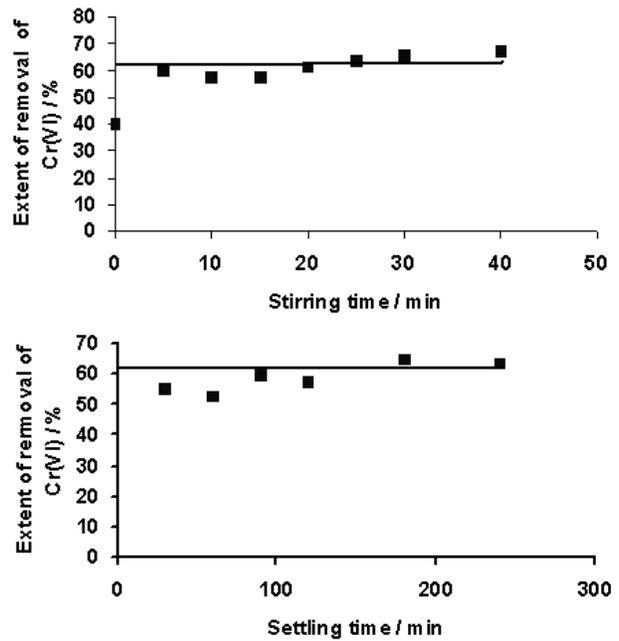
**Figure 2:** Extent of removal of Cr(VI) by fired brick particles at different settling time periods for 10 min stirring time ( $d < 1$  mm, 10 g brick clay fired at 400 °C, 100.0 cm<sup>3</sup> solution).

processes that take place during firing. The maximum removal of about 60% was observed for a firing temperature of 200 °C, as compared to 20% according to Figure 1. The significant enhancement of the affinity of brick clay toward Cr(VI) is probably due to the formation of carbon particles as a result of incomplete combustion of organic matter, such as humic acids, present in raw clay. As the Cr(VI) removal is improved by a factor of three when the firing temperature is changed from 400 °C to 200 °C, the latter temperature is more effective for Cr(VI) removal.

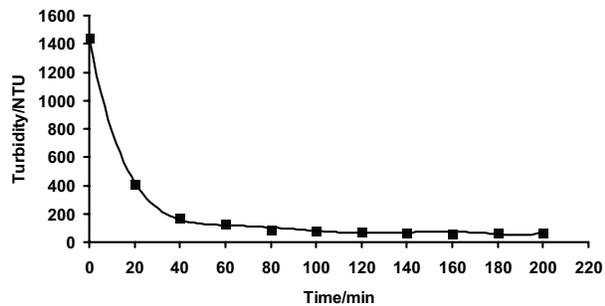
Turbidity of the clay suspensions is also an important parameter. Small particle sizes result in high turbidities and the metal ion adsorption/absorption is efficient. On the other hand, large particles do not lead to efficient metal ion removal. Particle sizes of  $d < 1.0$  mm were thus selected for all Cr(VI) removal studies as a compromise between enhanced turbidity values and the efficient transfer of Cr(VI) species from solution phase to the solid phase. In addition, turbidity of brick particle - Cr(VI) suspensions also depends on the nature of clay, which depends on the firing temperature.



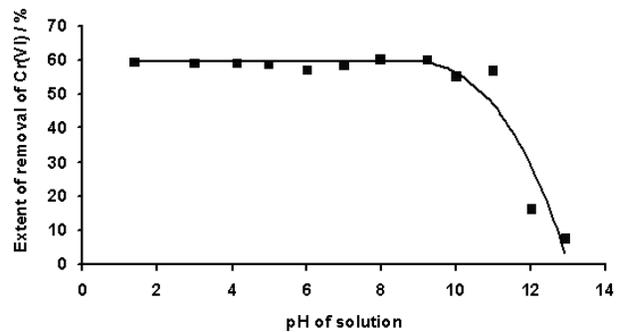
**Figure 3:** Extent of removal of Cr(VI) by brick clay fired at different temperatures (top) and corresponding turbidity values of the supernatant solution as a function of firing temperature (bottom) ( $d < 1$  mm, 10 g fired brick, 100.0 cm<sup>3</sup> solution, 10 min stirring time, 2 h settling time).



**Figure 4:** Extent of removal of Cr(VI) by brick particles at different stirring times for 2 h settling time (top) and different settling time periods for 10 min stirring time (bottom) ( $d < 1$  mm, 10 g brick clay fired at 200 °C, 100.0 cm<sup>3</sup> solution).



**Figure 5:** Variation of turbidity of the supernatant solution of brick particle - Cr(VI) suspension with settling time ( $d < 1$  mm, 10 g brick clay fired at 200 °C, 100.0 cm<sup>3</sup> solution, 10 min stirring time).



**Figure 6:** Extent of removal of Cr(VI) at different solution pH ( $d < 1$  mm, 10 g brick clay fired at 200 °C, 100.0 cm<sup>3</sup> solution, 10 min stirring time, 2 h settling time).

When the variation of the turbidity of fired brick particle - Cr(VI) suspensions is viewed as a function of firing temperature, a decreasing trend is observed initially (Figure 3). The lower turbidity observed with brick clay particles fired beyond 200 °C is associated with increase in the sedimentation rate of clay particles, which is directly proportional to the density difference between the fluid and the solid particle, and the square of the diameter of the solid, as shown in Equation 2<sup>22</sup>.

$$\text{Rate of sedimentation} = \frac{gD^2(d_1 - d_2)}{18\eta} \quad \dots (2)$$

where  $g$  is the acceleration of gravity,  $D$  is the particle diameter,  $d_1$  is the density of brick,  $d_2$  is the density of water and  $\eta$  is the viscosity of the medium. It has already been reported that the surface area of brick particles is significantly decreased when the firing temperature is increased<sup>19</sup>. This indicates that the particle size is increased with firing temperature affecting the rate of sedimentation according to Equation (2). In addition to the effect of the particle size, it is proposed that the presence of carbon particles formed is also responsible for decreasing turbidity of brick clay suspensions prepared with clay fired at temperatures above 100 °C, indicating the complexity of the sedimentation process. These carbon particles become activated with increased firing temperature and promote adsorption, resulting in low turbidity values. At elevated firing temperatures, above 600 °C, carbon particles are oxidized and leave the brick matrix resulting in increased turbidity again. In addition to the changes stated above, other chemical, physical or phase changes would also make contributions to change the turbidity of clay-water suspensions. Considering both extent of removal and turbidity measurements, it can be concluded that the optimum firing temperature for the highest removal and the lowest turbidity, the two opposing effects for effective removal, is 200 °C. All subsequent experiments were thus performed with brick clay fired at this temperature.

After optimization of the firing temperature for effective removal of Cr(VI), readjustment of periods of stirring and settling would be a necessity. Thus, the removal of Cr(VI) by brick clay fired at 200 °C was monitored by varying the above parameters (Figure 4). As the extent of removal is not much dependent on periods of stirring and settling, similar to the situation with brick clay fired at 400 °C, it can be argued that the parameters adjusted for brick clay fired at 400 °C are still valid for clay fired at 200 °C.

Additionally, the turbidity of supernatant solutions of brick particle - Cr(VI) suspensions with brick clay fired at 200 °C monitored for a period of over 3 hours

indicates that it exponentially decreases, and levels off to negligible values after 2 hours settling time period (Figure 5). This observation further supports the selection of 2 hours as the optimum period of settling time. The negative exponential variation of turbidity with time is indicative of the rate of sedimentation of brick particle - Cr(VI) suspensions being of first order. This aspect should also be considered in metal ion removal from industrial effluents.

Removal of Cr(VI) is not affected much by changing the solution pH from 1.4 up to about 11 (Figure 6). The sharp decrease beyond this pH is probably due to the presence of high OH<sup>-</sup> concentrations which would compete with Cr(VI), which is predominantly present as CrO<sub>4</sub><sup>2-</sup> in basic medium, for adsorption. As aqueous Cr(VI) solutions are approximately neutral, pH adjustment is not essential for effective removal of Cr(VI) unless the removal of other species that may be present in real samples needs such adjustments. Further, the presence of other ions, such as Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, which are commonly found in industrial effluents, do not influence the extent of Cr(VI) removal when both the interferent and Cr(VI) are present at 20 ppm level. Additionally, only a marginal decrease on the removal of Cr(VI) was observed when the ionic strength of the medium is increased up to 1.0 mol dm<sup>-3</sup> using KNO<sub>3</sub>. These observations indicate that the removal of Cr(VI) from aqueous medium does not need any ionic strength adjustments, and that the effect of the presence of interferents present in industrial effluents is minimal.

A glass column packed with brick pieces fired at 200 °C up to a length of 10 cm was able to remove more than 95% Cr(VI) during the initial treatment of 100 cm<sup>3</sup> aliquots of Cr(VI) solution. Passage of more aliquots decreases the removal ability due to saturation, and the total volume of Cr(VI) solution passed to reach a concentration of 70% of the initial value (30% removal) is 1.8 dm<sup>3</sup>. It is however difficult to control the particle size throughout a dynamic experiment as the brick still shows clay behaviour due to the low firing temperature of 200 °C, resulting in low flow rates. It is proposed that clay fired at 200 °C be mixed with bigger particles, such as sand, to maintain adequate flow rates in real applications. These findings justify the extension of the proposed treatment methodology for real applications, including the treatment of industrial effluents.

The mechanism of the removal of Cr(VI) is a complex process, as there are many modes of interaction of Cr(VI) species with brick clay particles due to the presence of different minerals in clay. Although it is important to understand the mechanism, the goal of this research is to optimize experimental parameters for

efficient removal of Cr(VI). Investigation of the removal mechanism of Cr(VI) is the next logical step, and research in this direction is currently underway.

## CONCLUSION

The optimum experimental parameters for the removal of Cr(VI) from aqueous solution as determined through batch experiments are, 10 minutes duration of stirring time, 2 hour settling time period and ambient pH. The highest Cr(VI) removal determined with brick clay fired at 200 °C, and the lowest turbidity observed in the supernatant solutions prepared with brick clay fired at temperatures in the range of 200 - 600 °C, indicate that the optimum firing temperature for Cr(VI) removal is 200 °C. The turbidity of brick particle - Cr(VI) suspensions exponentially decreases, levelling off at negligible values after a 2 hour settling time period supporting the optimum settling time period as stated above. Variation of the ionic strength of the medium and introduction of interferents commonly found in industrial effluents, such as Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, do not influence the extent of Cr(VI) removal. These findings suggest that proposed methodology has the potential in real applications. Ability of removing Cr(VI) under dynamic conditions provides additional support in this regard.

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