

EFFICIENCY OF LOW COST ADSORBENTS FOR THE REMOVAL OF ARSENIC FROM WATER

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ABSTRACT

Adsorption is one of the primary processes for removing arsenic from drinking water. This study focuses on developing inexpensive and effective adsorbents to remove arsenic from ground water. Eight different types of adsorbents were prepared. Some of these materials were chemically modified. The efficiency of percentage adsorption of arsenite, As(+III) on different materials were investigated at different pH, contact time and initial concentrations. Out of eight different types of adsorbents, the iron-loaded xanthated orange waste (Fe-XOW) showed high efficiency for the removal of arsenic. It was found that approximately 83 % of arsenite, As(+III) and 87% of arsenate, As(+V) removal could be achieved at optimum pH of 10 and 4 respectively. The significant effect of pH was in the range of 9 to 12 for As (+III) and 3 to 5 for As (+V). Time dependency experiments for the arsenite uptake showed that the adsorption rate on Fe-XOW was fast initially for 1 hour, followed by slow attainment of equilibrium at 2.15 hour. Adsorption isotherm test showed that equilibrium adsorption data were better represented by Langmuir model than the Freundlich model and the maximum adsorption (q_{max}) for As (+III) onto Fe-XOW was found to be 53.47 mg/gm. The concentration of arsenic in water sample was determined by standard silver diethyldithiocarbamate spectrophotometric method (SDDC method).

Key words: arsenate, arsenite, xanthated orange waste, adsorption.

INTRODUCTION

Arsenic occurs widely in nature and is best known for its toxic properties. Arsenic occurs in four different oxidation states (-III, 0, +III and +V) but in natural water it is mostly found in inorganic form as oxyanions of trivalent arsenite, (As^{3+}) or pentavalent arsenate, (As^{5+}). Arsenite is more toxic, mobile and more stable than arsenate in aqueous solution especially at pH greater than 7. Hence it is difficult to remove arsenite as compared to arsenate due to higher stability in natural water by simple adsorption and precipitation processes (Nagarnaik, 2002). Although there is no widely accepted mechanism of the release of arsenic in ground water but it has been accepted that most of all including in Nepal is of natural geological origin (Panthi, *et al.*, 2006).

Drinking arsenic rich water over a long period can result in various adverse health effects including skin problems, skin cancer, cancers of bladder, kidneys and lungs, disease of the blood vessels of the legs and feet, and possibly also diabetes, high blood pressure and reproductive disorders. Arsenic

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contamination of drinking water resources is a global crisis. However, this problem is more acute in countries like Bangladesh, India, Taiwan, China and Terai belt of Nepal (Pokhrel et al. 2009, Bissen *et al.*, 2000). Therefore, processes to remove arsenic from drinking water are urgently required.

Numerous arsenic removal technologies such as co-precipitation, liquid-liquid extraction, ion exchange, ultrafiltration, adsorption etc. have been so far used for arsenic removal. Among them, adsorption methods are considered to be most promising technologies because of simplicity to operate and cost effective. Many attempts have been made regarding the removal of arsenite and arsenate by using iron(III) loaded chelating ion exchange resins having their acidic or basic moiety as functional group. But treatments with the resins are expensive and not affordable to the people of developing countries (Biwas *et al.*, 2008, Ghimire et al. 2003). In this regard, efficiency of some low cost adsorbents prepared from some cheap biomasses and other materials for the removal of arsenite and arsenate from aqueous solution have been investigated in this work.

METHODOLOGY

All chemicals, As_2O_3 , $[Pb(CH_3COO)_2]$, $SnCl_2 \cdot 2H_2O$, $Na_2HAsO_4 \cdot 7H_2O$, C_4H_9NO , $FeCl_3$ used were of reagent grade. Silver diethyldithiocarbamate was of A.R. grade which was used without any further purification.

PREPARATION OF ADSORBENTS

Unmodified adsorbents

About 1 g of hematite was taken and it was converted into fine powder form and dried in hot air oven at about $80^\circ C$ for an hour. The fine powdered form of brick red (BR) and red mud (RM) was prepared as hematite.

Modified adsorbents

Iron (III)-loaded rice husk (Fe-RH)

Fresh rice husk was collected from a local rice mill and was passed through different sieve size. The fraction of particle between 425 and 600 μm (geometric mean size: 505 μm) was selected. Rice husk was washed thoroughly with distilled water and was dried at $60^\circ C$. The material thus obtained was designated as raw rice husk. For modification, the dried and sieved rice husk was treated with HNO_3 in 1:2 ratios, and 3 gm of acid treated rice husk was mixed with 500 mL of 1.5×10^{-2} M Fe (III) solution having pH 3 and stirred in rotary shaker at room temperature for 24 hours. The product (designated as Fe-RH) was washed with water until neutral and dried for 24 hour at $40^\circ C$ (Ong *et al.*, 2007).

Iron (III)-loaded sugarcane bagasse (Fe-SCB)

Raw sugarcane bagasse was collected from the juice center. It was cut into small pieces, washed several times with distilled water and dried in an oven at $100^\circ C$ for 24 hours. The adsorbent was then grinded and sieved to get the desired particle size of 300 to 425 μm and subjected to acid modification with H_2SO_4 in 1:2 ratios. The iron (III) was loaded using the same procedure as in the case of rice husk.

Iron Coated Sand (Fe-CS)

200 gm of sand was immersed in an acid (20% HCl) solution for 24 hour and was dried. Acid treated sand was mixed with 2M ferric chloride (80 mL) and

10 M sodium hydroxide (4 mL). The product (designated as Fe-S) was heated in an oven at 110°C for 14 hour and washed with distilled water until neutral and then dried for 24 hours at 40°C (Vithanage *et al.*, 2007).

Fe (III)-loaded xanthated orange waste (Fe-XOW)

Orange waste after juicing were collected from juice centre and crushed into small size. The crushed orange wastes were dried in an oven for 48 hours at 70°C. The dried wastes were further grounded into small sizes.

For the modification, the dried raw orange waste (20 gm) was treated with 50 mL of 18 % NaOH and stirred for 1 hour then 10 mL of CS₂ was added and the mixture was stirred in rotary shaker at room temperature for 24h. Thus obtained product was washed with water until neutral and dried for 24 hour at 40°C and sieved to obtain uniform particle size. The adsorbent now hereafter called as XOW-gel. Then iron (III) was loaded on XOW-gel (Fe-XOW) following the same procedure as in the case of rice husk (Ghimire *et al.*, 2002).

Fe (III)-loaded xanthated apple waste (Fe-XAW)

Apple waste after juicing were collected and crushed into small size. The crushed apple wastes were dried in an oven for 48 hours at 70°C. The dried wastes were further grounded into small sizes. It was then chemically modified and iron (III) was loaded as in the case of orange waste adsorbent. The adsorbent now hereafter called as Fe-XAW.

Adsorption studies

Effect of pH on arsenic removal

Adsorption of arsenic as a function of pH was examined in a series of experiments where the initial concentration was maintained constant (2 mg/L) at varying pH from 2-12. pH of the solution was adjusted by adding small amount of NaOH (1M) or HCl (1M). From such experiments, the optimum pH value for arsenic (III and V) adsorption onto the adsorbents was obtained. All batch adsorption experiments were carried out in 125 mL stoppered bottles with 25 mg of the adsorbents with 25 mL of initial working solution of arsenic. The bottles were then agitated on a rotary shaker at room temperature for 24 hours. After 24h, the suspensions were filtered immediately and the filtrate was analyzed for arsenic concentration. The concentrations of arsenic before and after adsorption were determined by Silver Diethyldithiocarbamate Spectrophotometric Method (SDDC method). Absorbance was recorded by using WPA S-104 spectrophotometer (UK) using 1 cm glass cuvette. From arsenic concentrations measured before and after the adsorption (C_o and C_e , respectively) and dry weight of adsorbent (W), as well as volume of aqueous solution (V), the amount of arsenic adsorbed (q) was calculated according to the equation

$$q = \frac{C_o - C_e}{W} \times V \text{ (mg/g)}$$

The removal percentage (R %) was calculated according to the equation

$$R \text{ (%) } = \frac{C_o - C_e}{C_o} \times 100$$

The pH of the solution before and after the adsorption was adjusted and monitored using Digital pH meter (WPA CD 300).

Effect of contact time on arsenic removal

After determining the optimum pH, equilibrium time for adsorption of arsenite onto Fe-XOW was studied at optimum pH and room temperature. For this 25 mL of 2 mg/L of arsenite solution was taken in a 125 mL stoppered bottle with 25 mg of adsorbent. The suspension was equilibrated in a mechanical shaker for different time intervals from 15 to 150 minutes. The suspensions were then filtered immediately and analyzed by SDDC method.

Isotherm Studies

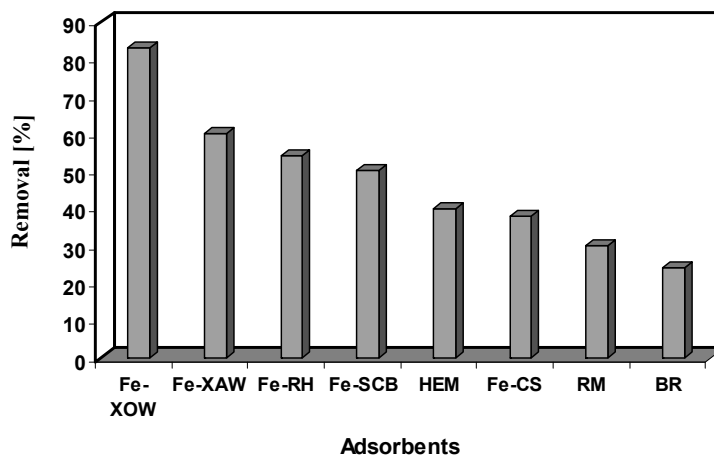
The isotherm studies were conducted at room temperature by varying the initial concentration of arsenic solutions ranging from 5 mg/L to 250 mg/L. The adsorptions were carried out by shaking 25 mL of arsenite solution with 25 mg of Fe-XOW for 24 h in a mechanical shaker. The arsenic concentrations after adsorption were analyzed by SDDC method. This study helps in evaluating the maximum adsorption capacity of arsenic onto different low cost adsorbents.

RESULTS AND DISCUSSIONS

Effect of pH on adsorption of arsenite onto various chemically modified and unmodified adsorbents

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the adsorbent, so pH is an important parameter affecting the adsorption of metal ions from aqueous solution. Figure 1 shows the relationship between removal percentage and equilibrium pH on the adsorption of arsenite onto chemically modified and unmodified adsorbents at an initial concentration of 2 mg/L. The arsenite uptake by different types of chemically modified and unmodified adsorbents was found to be very sensitive to pH variation at the examined range of pH from 6-13. The removal of arsenite by adsorption onto different types of adsorbents was found to increase up to 83% in the highly alkaline medium.

Figure 1: Effect of pH on adsorption of arsenite onto various low cost adsorbents



From Figure 1 it is clear that out of eight different types of adsorbents Fe-XOW has high efficiency for the removal of arsenic. About 83% of arsenite was adsorbed on the Fe-XOW at optimum pH of 10. While only 60, 54, 50, 40, 38, 30 and 24% of arsenite adsorption was found onto the Fe (III)-loaded xanthated apple waste (Fe-XAW), Fe (III)-loaded rice husk (Fe-RH), Fe (III)-loaded sugarcane bagasse (Fe-SCB), hematite (HEM), Fe-coated sand (Fe-CS), red mud (RM) and brick red (BR) at optimum pH of 10, 12, 12, 12, 12, 12 and 10 respectively.

Figure 2: Comparison of adsorption of arsenite onto various adsorbents at optimum pH

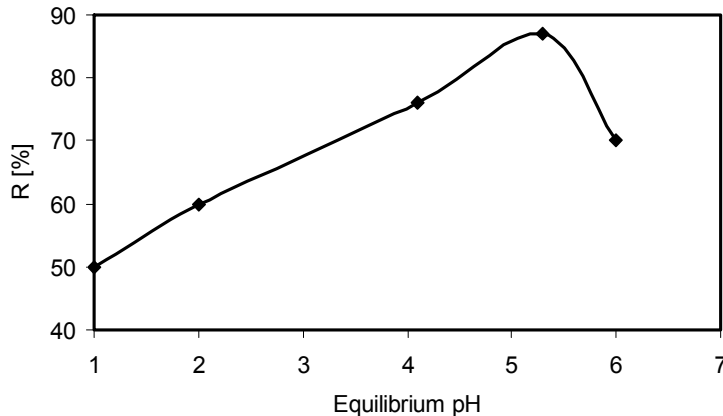


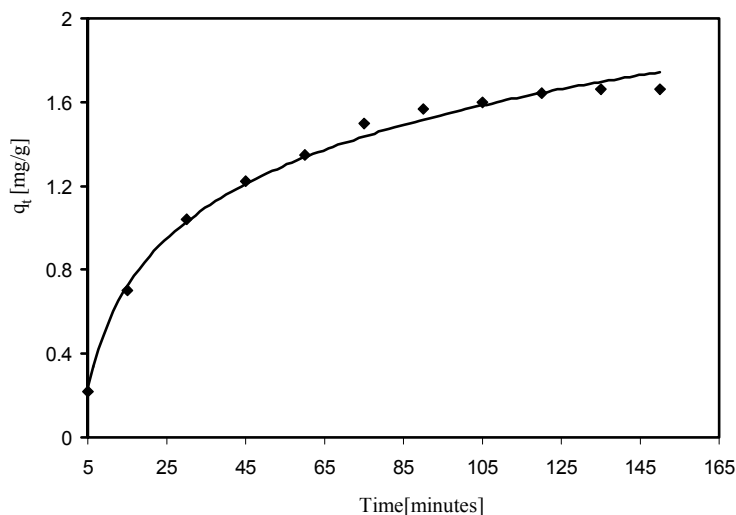
Figure 2 shows the results of comparative studies of removal [%] of arsenite by various modified and unmodified adsorbents. The adsorption

increases rapidly near the optimum pH range hence pH of solution has significant effect on the adsorption of arsenite.

Effect of pH on adsorption of arsenate onto Fe-loaded xanthated orange waste (Fe-XOW)

Figure 3 shows the adsorption of arsenate onto Fe-XOW at an initial concentration of 2 mg/L. The pH of solution plays an important role for adsorption. It is considered that Fe (III) is adsorbed by releasing protons from the phosphorylated unit of cellulose according to cation exchange mechanism. The adsorbed iron will co-ordinate octahedrally with hydroxyl ions and neutral water molecules that are available in aqueous medium.

Figure 3: Effect of pH for adsorption of arsenate onto Fe(III)-loaded XOW

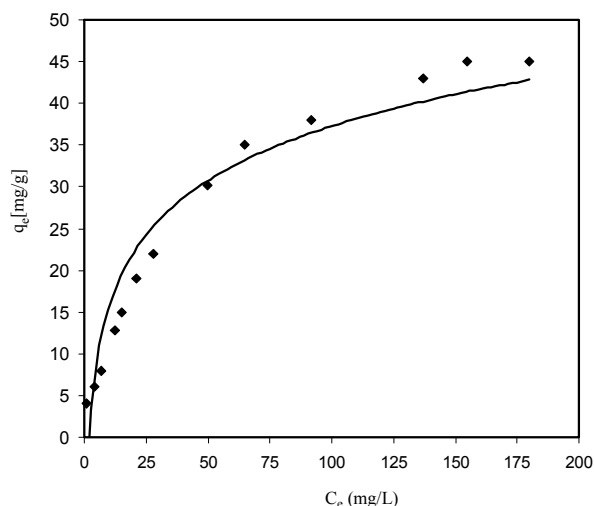


The adsorption of arsenic will take place by releasing hydroxyl anion from the above mentioned co-ordination sphere. For this reason, the adsorption of arsenic species onto Fe-XOW is termed as ligand exchange adsorption. But the fate is decided only in the presence of Fe (III). This is the reason why Fe (III)-loaded materials are being used for arsenic removal (Ghimire *et al.*, 2000). It is clear from the Figure 3 that approximately 87% of arsenate was adsorbed onto the Fe-XOW at an initial concentration of 2 mg/L at optimum pH of 4. Optimum adsorption of arsenate was observed in acidic medium, whereas arsenite adsorption was found in weakly alkaline medium.

Equilibrium time studies

Figure 4 shows the adsorption of arsenite onto Fe-XOW from 15 to 150 minutes (2.5 h). The adsorption of arsenite was found to be constant after 2.15h. Thus the required equilibrium time for the adsorption of arsenite onto Fe-XOW was 2.15 h. Time dependency experiments for the arsenite uptake showed that the adsorption rate on Fe- XOW was fast initially for 1 hour, followed by slow attainment of equilibrium at 2.15 hours.

Figure 4: Effect of contact time on adsorption of arsenite onto Fe-XOW



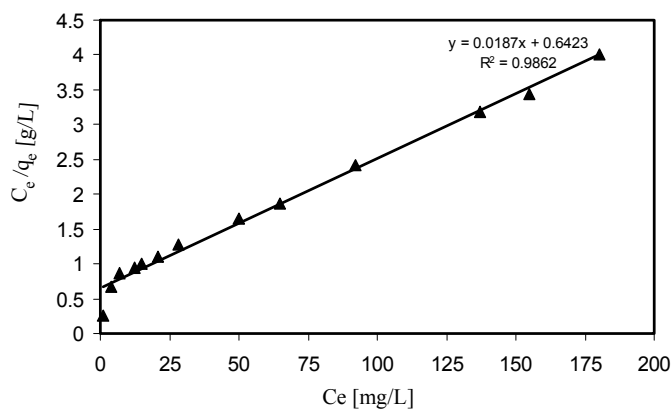
The arsenic adsorption capacity is rapid initially because of the presence of large number of anion exchange sites. When all the active sites are occupied by arsenite then adsorption remains constant.

Isotherm studies

The main objective of isotherm study is to evaluate the capacity of the modified adsorbents to sequester As(III) from an aqueous solution. It was done by characterizing the equilibrium state of the Fe-XOW adsorbent that has been allowed to react with aqueous solution of As(III).

Figure 5 shows the adsorption isotherm for As(III) onto the Fe-XOW. It is seen that the adsorption of As (III) increases with the increase in equilibrium arsenite concentration.

Figure 5: Adsorption isotherm of arsenite by Fe-XOW



Uptake of arsenite is eventually limited by the constant number of active sites and resulting plateau of isotherm. This is because, at lower arsenite concentration, the ratio of the initial moles of arsenite to the available surface functional group is low, but at higher concentration, the available functional sites of the adsorbent become fewer compared to the moles of arsenite present and hence the uptake of metal ion becomes independent upon the initial metal ion concentration.

Adsorption isotherm model

Adsorption of As(III) onto Fe-XOW gives the linear relationship with Langmuir and Freundlich isotherms which are shown in Figure 6 and 7. Langmuir and Freundlich parameters are determined from the slope and intercept of the plots of c_e/q_e versus c_e and $\log q_e$ versus $\log c_e$ respectively.

Figure: 6 Langmuir isotherm plot for adsorption of arsenite onto Fe- XOW

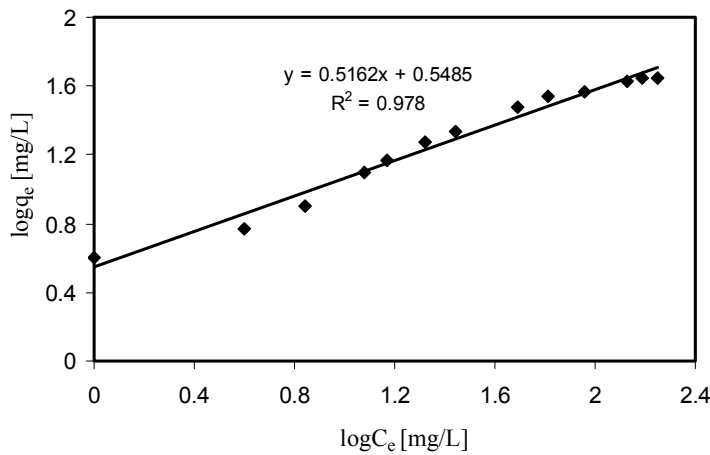
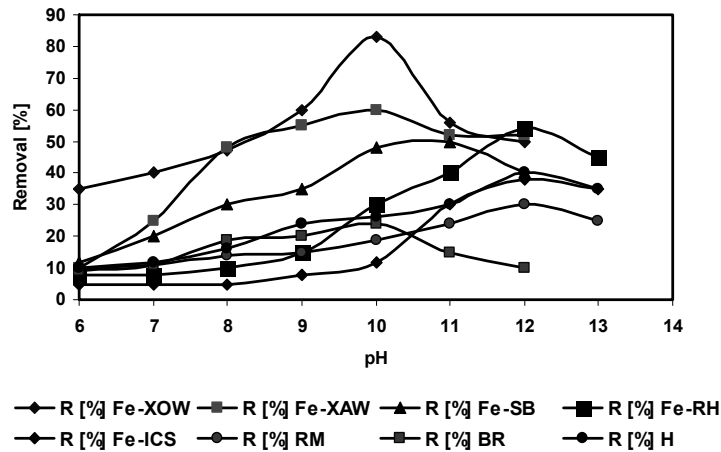


Figure 7: Freundlich isotherm plot for adsorption of arsenite onto Fe-XOW



The results obtained are presented in the Table 1. A comparatively high value of correlation coefficient for Langmuir adsorption as compared to Freundlich adsorption isotherm indicates that the adsorption process more closely fits to the Langmuir isotherm model.

Table 1: Langmuir and Freundlich adsorption isotherm parameters and correlation coefficient with experimental q_{max}

Langmuir isotherm			Experimenta l $q_{max}(mg/g)$	Freundlich isotherm		
$q_{max}(mg/g)$	$b(L/mg)$	R^2		$K(mg/g)$	$1/n$	R^2
53.47	0.642	0.986	48.00	3.535	0.516	0.978

The more favorable adsorbent is indicated by the higher value of slope of an isotherm. From the slope, the maximum adsorption capacity of Fe –XOW was found to be 53.47 mg/g for As(III).

Analysis of Sample Water of Nawalparasi and Rupandehi Districts

The natural water samples collected from different tube wells of Devdaha VDC of Rupandehi District and Jahada and Manahari VDC of Nawalparasi district were analysed for arsenic content by silver diethyldithiocarbamate spectrophotometric method (SDDC). Then samples were subjected to adsorbent treatment with Fe-XOW. The results of the analysis were presented in the Table 2.

Table 2: Arsenic concentration in water samples determined by silver diethyldithiocarbamate spectrophotometric (SDDC) method

Sample No.	Districts	VDC	Initial concentration (ppb)	Equilibrium concentration (ppb)	% Adsorption of arsenic
A	Nawalparasi	Manahari	360	180	50
B	Nawalparasi	Jahada	250	120	52
C	Nawalparasi	Jahada	300	135	55
D	Rupandehi	Devdaha	400	200	50
E	Rupandehi	Devdaha	230	92	60
F	Rupandehi	Devdaha	350	161	54

The results show that only 50–60% of arsenic removal was achieved from the collected water samples which is less than arsenic removal from the synthetic solution. This low arsenic removal from the water sample may be due to the competitive adsorption of arsenic, phosphate, silicate and other ions present in the water samples.

CONCLUSION

In this study different types of chemically modified and unmodified adsorbents were prepared and their efficiency for the removal of arsenic [III and V] from water was analyzed. The effect of pH in the adsorption of arsenite onto chemically modified and unmodified adsorbents at an initial concentration of 2 mg/L was investigated. The adsorption of arsenic was dependent on pH of solution, initial concentration of adsorbate and contact time. The pH of the

solution has shown to be one of the key variables for arsenic removal. It was found that out of eight different types of adsorbents Fe-XOW has high efficiency for the removal of arsenic from water. It adsorbed approximately 83% of total arsenite and 87% of arsenate present in the water at optimum pH of 10 and 4 respectively. The equilibration time and maximum adsorption (q_{max}) for the adsorption of arsenite onto the Fe-XOW was found to be 2.15 hour and 53.47 mg/gm respectively.

Arsenic content of water samples of Nawalparasi and Rupandehi district was analyzed by standard silver diethyldithiocarbamate spectrophotometric method (SDDC). The samples were subjected to adsorbent treatment with Fe-XOW for the removal of arsenic. Only 50– 60% of arsenic removal was achieved from the water sample which is less than arsenic removal from the synthetic solution. This low arsenic removal from the water samples may be due to the competitive adsorption of arsenic, phosphate, silicate and other ions present in the water samples.

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