

STUDIES ON THE FERRIC IRON SORPTION FROM ACID MINE DRAINAGE ON LEWATIT RESIN AS A STEP FOR METAL CONVERSION TO A VALUE-ADDED PRODUCT

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ABSTRACT. The study aimed to determine the optimal conditions for adsorption and elution of iron from acid mine drainage by ion-exchange resin LEWATIT MonoPlus TP 207 under a batch regime of operation. Langmuir's sorption equation was employed to analyse the equilibrium data from the experiments. The data fitting demonstrated that the process obeyed pseudo-second-order kinetics with a linear regression coefficient (R^2) of 0.9999. Because of the higher demand for hydrochloric solution (100 g/L) for the ferric iron elution, we studied the effect of the preliminary stage of galvanic elution of Fe(III) to Fe(II) in the presence of H_2 . In that way, a slightly acidic solution (30 g/L) was sufficient to desorb more than 95 % of iron from ion exchange resin LEWATIT MonoPlus TP 207 at a temperature of 70 °C.

Keywords: iron, LEWATIT, sorption, reductive elution

Introduction

As one of the most abundant chemical elements in the Earth's crust, iron raises a need for adequate control in mining and metallurgical industries. Furthermore, because of its existence in two valency states (ferrous and ferric), both well soluble at acidic pH, iron plays a crucial role in the hydrometallurgical recovery of non-ferrous metals, radioactive elements, precious elements. Higher demand for the groups mentioned above, plus rare-earth metals, was determined by the constant annual growth of the electronic industry mainly. Recent studies showed that some biological and chemical methods could be combined, and thus, it would be possible not only to process raw materials and industrial wastes with complex mineralogy but also to adapt technologies to the stricter environmental regulation (Parhi et al., 2015, Georgiev et al., 2018, Dev et al., 2020).

Mining and metallurgical industries are among industrial branches, which lead to higher iron concentration in freshwater. Consequently, it has both direct and indirect effects on freshwater ecosystems (Vuori, 1995). The direct effects are a consequence of the toxic action of iron compounds (soluble and/or minerals) on the species growth, reproduction, and survival. The indirect effects result from the limited access of organisms to a peculiar ecosystem's resource, characterised by the relevant quality and quantity.

Three different techniques are applied to control the iron content in laden leach liquors (LLL) and wastewater (Georgiev et al., 2020). The methods for iron precipitation are still the methods most widely applied at industrial scale. The main aim is to precipitate iron to non-toxic ferric iron oxyhydroxide with a crystalline structure and reasonable filtration rate. The main disadvantage is the losses of some valuable metals (up to 13 – 15 %) when the approach is applied to LLL. Magnetite synthesis as a method for iron removal and recovery from solutions is the most promising. The reason for that is the existence of different routes and techniques for mineral synthesis, which strongly affect their particle size, shape, surface, optical and magnetic properties (Kulkarni et al., 2014). It enables the application of magnetite in various fields, ranging from magnetic data storage, biosensing, biomedicine and drug delivery to nano-sorbents in environmental engineering.

Regarding wastewater treatment, especially generated from abandoned mines, the so-called passive system is applied. It is based on chemical and biological processes carried out at an ambient temperature and pressure and iron precipitates as

different minerals depending on the maintained environmental conditions (Groudev, 2008).

The other two approaches are based on using highly selective reagents towards some valuable elements from LLL, which enabled their preferential sorption, concentration and elution in its stream lately. The process of solvent extraction relies on a mixture of appropriate diluents (such as kerosene) and suitable organic compounds (some of the organo-phosphorous acids), which form a strong bond with ferric iron from leach liquor (Azizorghaben et al., 2016). The ion exchange process is an alternative to solvent extraction, and the use of ion-exchange resins prepared from a wide range of synthetic polymers is the basis for this. It determines the ability to produce a wide range of ion exchange resins, each with a specific surface group and charge to adsorb the relevant substance selectively. The first application of ion exchange resins in hydrometallurgy was for uranium recovery from LLL. After developing chelating and impregnated ion exchange resins, their application increased significantly, especially in copper recovery (Davenport et al., 2002). Nowadays, ion exchange resins are applied for non-ferrous, precious, and palladium group metals' recovery (Ashiq et al., 2019).

LEWATIT ion exchange resins are commercial products widely used in practice for dealkalisation, softening, demineralisation of natural and industrial waters, catalysis and processing of different organic compounds to produce foods or biodiesel (Product Guide, 2021). The presence of aminophosphonic groups on the resin matrix and a negative surface charge determine its ability to extract non-ferrous metals selectively, even from solutions enriched with inorganic and organic compounds with excellent complexing properties – ammonia, aliphatic and aromatic amines, carboxylic acids, diphosphates, or polyphosphates. The regeneration of ion exchange resin with a suitable inorganic acid starts when more than 75-80 % of its sorption capacity is saturated. In this way, already sorbed non-ferrous metals are desorbed and concentrated in solution with a volume considerably lower than the initial volume of solution (Waltling, 2006). The main advantages of using the ion-exchange process for metals recovery are its easiness of operation, no reagent losses, no phases of disengagement, and the lower risk to human health (Nikoloski, Ang, 2014).

This study aimed to determine the optimal conditions for adsorption and elution of iron from acid mine drainage by ion-exchange resin LEWATIT MonoPlus TP 207 under a batch regime of operation.

Materials and methods

Acid mine drainage (AMD) from an abandoned copper mine in Northwest Bulgaria was sampled and analysed in the laboratory. The chemical content and properties of the solution are presented in Table 1.

Effect of the preliminary iron oxidation and precipitation on the ferric iron adsorption by ion exchange resin LEWATIT

The chemical oxidation of ferrous iron was carried out with the serial addition of hydrogen peroxide (30 % solution) and Na_2CO_3 combined with intensive sparging of the solution with air until the pH value in the range of 2.5 – 3.75 is reached. WTW pH-meters equipped with pH-glass and Eh electrodes, assembled with Ag/ AgCl reference system and Pt wire, respectively, were used to measure pH and Eh during the chemical oxidation and neutralisation processes. Batch tests for iron sorption were carried out in polypropylene beakers with a volume of 250 mL. LEWATIT MonoPlus TP 207, weak acidic macroporous cation exchange resin with mean bead size 0.61 (± 0.05) mm, was the ion exchange resin used in the study. Initially, 20 g of ion exchange resin was activated with a 100 mL solution containing 100 g/ L acid. The stirring rate was 300 rpm, duration – 10 minutes. After the solution separation, the resin washing with water extracted the non-consumed acid. Iron sorption started by adding 100 mL of acid mine drainage solution, preliminary treated by chemical oxidation and neutralisation, to the already activated ion exchange resin. The standard conditions for iron adsorption, which applied during the batch tests, if other conditions are not mentioned, were as follows: 300 rpm, 30 °C, aqueous : resin ratio (A : R) = 5:1, agitation time of 10 minutes. A water bath maintained a constant temperature during the experiment. pH equilibrium (pH_{eq}) was measured at the end of the sorption processes. The calculation of iron sorption (D) percentage was according to the equation:

$$D, \% = (C_0 - C_e / C_0) \times 100 \quad (1)$$

where: C_0 and C_e are the initial and equilibrium iron concentration in the solution before and after sorption (in mg/L), respectively.

Table 1. Chemical content of acid mine drainage

Index	Value
pH	2.26
Eh, mV	445
Acidity, mmol/ L	76.3
Fe, mg/ L	3345
Cu, mg/ L	137
Zn, mg/ L	311
Al, mg/ L	183
SO_4^{2-}	3775

The equilibrium iron content on the ion exchange resin (q_e , mg/g resin) was found according to the equation:

$$q_e = (C_i - C_e) \times V / w \quad (2)$$

where: V – a volume of the solution during the sorption test, L; w – the weight of the ion exchange resin, g.

The distribution coefficient (K_d , L/g) of ions between the resin and solution at an equilibrium was quantified by:

$$K_d = q_e / C_e \quad (3)$$

The separation factor (β) between two ions was quantified by:

$$\beta = K_{d1} / K_{d2} \quad (4)$$

where: K_{d1} and K_{d2} were the distribution coefficient of two ions contained in the solution.

A Langmuir sorption equation was employed to analyse the iron equilibrium data at conditions (pH and temperature) optimal for iron sorption:

$$1/q_e = [1/(K_L \times q_{\text{max}})] \times (1/ C_e) + 1/ q_{\text{max}}, \quad (5)$$

where: q_{max} – maximum content of iron that could adsorb at the relevant experimental conditions, mg/ g ion exchange resin, K_L – constant, L /g. q_{max} and K_L were calculated according to the following equation:

$$q_{\text{max}} = 1/ \text{interception point} \quad (6)$$

$$K_L = 1/ (\text{slope} \times q_{\text{max}}) \quad (7)$$

where: interception point and the slope were the parameters of a line of $1/ C_e$ versus $1/q_e$.

First and second-order rate equations evaluated the effect of pH and temperature on the iron sorption on ion exchange resin LEWATIT (Ho et al., 2000).

Iron desorption from loaded ion exchange resin LEWATIT MonoPlus TP 207

The iron desorption from the loaded ion exchange resin Lewatit MonoPlus TP 207 was studied at oxidative or reductive conditions. The desorption agent at oxidative conditions consisted of hydrochloric acid with a concentration of 60 – 120 g/ L. Aqueous : resin ratio (A:R) applied for the iron desorption was in the range of 2.5 : 1 to 1.5 : 1, and the other conditions were the same as the conditions described for iron sorption.

The reductive elution of iron was carried out in the presence of H_2 , and it took place in a tightly closed three-necked flask that contained the resin loaded with iron. The diluted acid solution (20 – 60 g HCl/ L) was added to the flask after oxygen removal by sparging with N_2 . In order to ensure Fe^{3+} reduction to Fe^{2+} , the galvanic iron elution was carried out by the flask sparging with H_2 . A water bath maintained a constant temperature during the process. The duration of the reductive elution was in the range of 20 – 40 minutes.

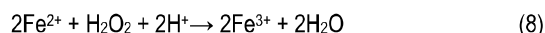
Copper ammonia method was used for the copper content determination of the solutions. The selective complexation of ferrous and total iron with 5-sulfosalicylic acid at acidic and alkaline pH determined the ferrous and ferric iron concentration at acidic and alkaline pH (APHA, 1995). The intensity of formed complexes was measured at the relevant wavelengths by spectrophotometer MERCK SQ22.

Results and discussion

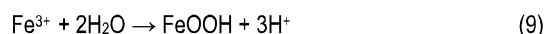
Iron concentration in acid mine drainage was higher than the concentration of other metals present in the solution. The ferrous ion was the main iron valency state in the tested solution because the solution drained through the ore body, and the low

concentration of molecular oxygen limited the activity of indigenous chemolithotrophic bacteria with iron-oxidising ability.

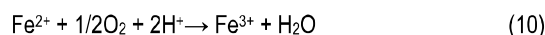
It is well-known that ion exchange resins adsorb ferrous ions non-selectively, and the process is not efficient in the presence of other divalent cations, especially copper and zinc (Fatima et al., 2020). For that reason, preliminary chemical oxidation and neutralisation of AMD was applied to oxidise the ferrous ions into a ferric state. H_2O_2 was used, and we calculated its amount according to the reaction:



Sodium carbonate was added as an alkalisng agent to the solution when redox potential was higher than + 550 (mV). It enhanced the ferric iron precipitation mainly as goethite (β -FeOOH):



At pH > 3.00, the intensive sparging of the pulp with air enhanced the chemical oxidation of the residual concentration of ferrous iron:



The final pH point of chemical neutralisation significantly affected the ferric iron adsorption by ion exchange resin (Table 2). For example, the lowest equilibrium concentration of iron in solution after the adsorption was measured when the final pH of neutralisation was 3.5. Furthermore, further addition of alkalisng agent during the chemical neutralisation negatively affected the iron adsorption due to the enhanced adsorption of other cations from the solution.

Initially, the chelating resin adsorbed bivalent cations present in the solution. This process acted as a source of hydrogen ions from the resin to the solution, which initiated the goethite dissolution and ferric iron ions accumulated into the solution:

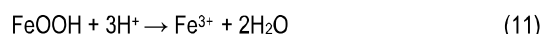


Table 2. *Effect of the equilibrium pH on the iron sorption on ion-exchange resin LEWATIT MonoPlus TP 207**

pH of AMD after chemical oxidation and neutralisation	Equilibrium pH	Equilibrium concentration of iron, C_e , mg/ L	Equilibrium concentration of copper, C_e , mg/ L
2.50	1.23	481.5	24.1
3.00	1.48	291	16.2
3.50	1.63	40	12.2
3.75	1.91	112.5	9.5

* All experiments were carried out at a temperature of 30 °C

The higher charge of ferric ions enhanced their selective adsorption on the surface of chelating resin compared with the adsorption of presented bivalent cations. At such conditions, the reaction could describe the ferric iron adsorption on chelating resin and the following ion exchange with hydrogen ions:

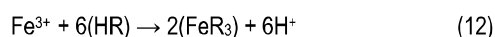


Table 3. *Effect of the equilibrium pH on the separation between iron and copper adsorption on ion-exchange resin LEWATIT MonoPlus TP 207**

Equilibrium pH	Distribution coefficient of iron, K_{d1} , L/ g	Distribution coefficient of copper, K_{d2} , L/ g	Separation factor (β), K_{d1}/ K_{d2}
1.23	0.30	0.22	1.36
1.48	0.52	0.36	1.44
1.63	4.13	0.49	8.43
1.91	1.44	0.65	2.21

* All experiments were carried out at a temperature of 30 °C

Table 4. *Effect of the temperature on the iron sorption on ion-exchange resin LEWATIT MonoPlus TP 207**

Temperature, °C	Equilibrium pH	Equilibrium concentration of iron C_e , mg/ L	Efficiency of iron sorption, %
10	1.17	625.3	81.3
20	1.2	347.8	89.6
30	1.63	40	98.8
40	1.61	50.2	98.5

R denotes that the resin organic part is not involved in the ion exchange.

Copper and zinc were the non-ferrous metals present in higher concentrations in the studied AMD, and the copper adsorbed to a greater extent at the tested experimental conditions (Table 2). Despite the aluminium concentration higher than the content of copper, it did not have an effect on the ferric iron adsorption, which was confirmed by Batelho Junior et al. (2019) results. The iron to copper adsorption steadily increased with the increase of pH equilibrium from 1.23 to 1.63.

Table 5. *Effect of the ion exchange resin's amount on the ferric iron sorption*

LEWATIT amount, g	C_e , mg/ L	q_e , mg/ g	The efficiency of iron adsorption, %
5	2515	16.60	24.8
10	1682	16.63	49.7
15	890	16.37	73.4
20	40	16.53	98.8
25	13.4	13.33	99.6

Table 6. *Kinetic parameters of iron adsorption on ion-exchange resin LEWATIT MonoPlus TP 207 determined by pseudo-first-order and pseudo-second-order equation rate*

Pseudo-first order equation rate				
Slope	Intercept	q_e , mg/ g	K_1 , min ⁻¹	R ²
-0.4289	2.2918	9.9827	-0.0429	0.8274
Pseudo-second order equation rate				
Slope	Intercept	q_e , mg/ g	K_2 , g.mg ⁻¹ .min ⁻¹	R ²
0.0556	0.049	17.9856	0.0631	0.9999

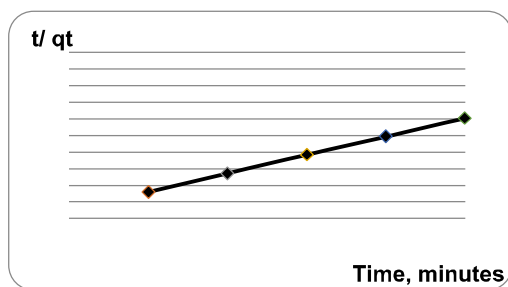


Fig. 1. Fitting of the experimental data to the pseudo-second-order kinetics

The distribution coefficients (K_d) values increased from 0.30 to 4.13 and from 0.22 to 0.40. At an equilibrium pH of 1.63, the separation factor (β) between ferric and copper ions was with the highest value (Table 3). The negative effect of the lower temperature on the iron adsorption (Table 4) could be compensated by a more prolonged process duration or an increase in the amount of the chelating resin used.

The studies about iron adsorption in the presence of different amounts of resin enabled the determination of the main adsorption process's characteristics through a Langmuir equation. For example, at the optimal conditions (equilibrium pH 1.63 and temperature of 30 °C), the calculated maximum ferric iron adsorbed on the resin was 16.6 mg/ g resin. Its value was almost equal to the experimentally determined equilibrium iron content (q_e) on the resin at the end of the adsorption process (16.53 mg/ g resin, Table 5). The distribution coefficient value of ferric iron (k_L) determined by the Langmuir equation was 3.87, and it was similar to the value of the distribution coefficient (k_d) determined experimentally (4.13, Table 3). Zhang et al. (2016) determined an almost equal value for q_{max} (16.33 mg Fe/ g resin) when studied the ferric iron extraction from synthetic copper solution with hydroxy-oxime chelating resin.

Table 7. Effect of the hydrochloric content on the iron elution from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

Content of HCl in desorption solution, g/L	Fe in solution, mg/ L	The efficiency of iron desorption, %
40	2405	36.4
60	4335	65.6
80	6160	93.2
100	6370	96.4

* All experiments were carried out at a temperature of 30 °C

Table 8. Effect of the hydrochloric content on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

Content of HCl in desorption solution, g/ L	Fe in solution, mg/ L	The efficiency of iron desorption, %
10	2150	32.5
20	4550	68.8
30	6370	96.4
40	6490	98.8

* All experiments were carried out at a temperature of 70 °C

Table 9. Effect of the temperature on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

Temperature, °C	Fe in solution, mg/L	The efficiency of iron desorption, %
30	3790	57.3
50	5260	79.6
60	5925	89.6
70	6370	96.4
80	6395	96.7

* HCl content in the desorption solution was 30 g/ L

Table 10. Effect of the duration on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

Duration, minutes	Fe in solution, mg/L	The efficiency of iron desorption, %
20	4840	73.3
30	6370	96.4
40	6488	98.2

* All experiments were carried out at a temperature of 70 °C and in the presence of 30 g HCl/L

Riveros (2004) has shown that the resins' ability to adsorb ferric iron strongly depends on their matrix morphology and the surface groups' acidity. For example, gel-type resins do not adsorb large amounts due to the very low rate of Fe^{3+} diffusion. In contrast to the macroporous acrylic resins, where that effect does not exist, ferric iron is extracted efficiently and selectively. The presence of other competitive cations also affects the resin adsorption capacity to iron. For example, a study carried out by Millar et al. (2015) showed that q_{max} of strong acid cation resin toward ferric iron from solution with no presence of other cations was higher than 47.1 mg/ g resin.

The results from kinetic experiments carried out at the optimal conditions for the iron adsorption show that the process better fits the pseudo-second-order equation rate.

Table 11. Effect of the aqueous: resin (A : R) ratio on the galvanic elution of iron from loaded ion-exchange resin LEWATIT MonoPlus TP 207*

Aqueous : resin (A : R) ratio	Fe in solution, mg/ L	The efficiency of iron desorption, %
2.5: 1	6550	99.1
2.0: 1	7285	88.2
1.5: 1	8135	74.2

* The duration of galvanic elution of iron for all experiments was 60 minutes

For example, the value of equilibrium iron content on the resin determined by that equation was 17.98 mg/ g resin (Table 6), compared to the experimentally determined value of 16.53 mg/ g. The linear regression coefficient (R^2) value was 0.9999, and the straight line that expressed the kinetic function of t versus t / q_t , passed through all experimentally determined dots (Figure 1). On the other hand, the value of equilibrium iron

content (q_e) determined by pseudo-first-order equation rate was 9.98 mg/ g.

Iron desorption from loaded ion-exchange resin LEWATIT

The opposite process – the process of the iron desorption took place in a solution with acidic pH (Table 7). Apart from the regeneration of the adsorptive properties of the chelating resin, the resin elution played a role in increasing ferric iron concentration in the solution multifold by decreasing the value of the applied aqueous: resin ratio. For that reason, the efficiency of iron desorption was a key parameter for the process characterisation. Therefore, we studied two approaches for the iron desorption from loaded ion-exchange resin LEWATIT MonoPlus TP 207 based on hydrochloric acid as a desorption agent. Hydrochloric acid was used because ferric iron precipitated as akaganeite (γ -FeOOH) in the next step after adding an alkalisng agent and pH correction to a value higher than 3.0. The akaganeite is a precursor for magnetite (Fe_3O_4) synthesis in an oxygen-free milieu and at an appropriate concentration of ferrous iron.

Iron desorption with a solution with a high content of HCl

The higher acid concentration in the desorption solution enabled breaking the chemical bonds between the adsorbed ferric iron ions and the negatively charged functional groups of the chelating resin to carry out at a higher rate. Therefore, the efficiency of iron desorption strongly depended on the acid concentration in the solution. For example, more than 90 % of iron desorbed when the concentration of hydrochloric acid in the desorption solution was higher than 75 g/ L (Table 7). The kinetic of iron desorption with a highly acidic solution was not temperature-dependent, and the process efficiency was acceptable to even at a temperature of 10 °C. However, the efficiency of iron desorption dropped significantly if the value of applied A: R was lower than 2.5 : 1. So, the ferric iron concentration from acid mine drainage increased twofold when ferric iron sorption on LEWATIT MonoPlus TP 207 resin was combined with a desorption stage in the presence of a desorption solution with higher hydrochloric acid content.

Galvanic elution of iron from the loaded ion-exchange resin LEWATIT

The second approach tested relied on the preliminary ferric iron reduction. A wide range of different reducing compounds – gaseous (SO_2 (Majima et al., 1985), H_2 (Demopoulos, Gefvert, 1984), organic (oxalic acid (Zhang et al., 2016)), and inorganic compounds (Zn^0 (Lupi, Pilone, 2000); $\text{S}_4\text{O}_6^{2-}$ (Batelho-Junior et al., 2019)) could be used for that purpose. H_2 was the reducing substance used in this study, and the main aim was to reduce ferric iron to ferrous state preliminary:



In that case, the functional groups of chelating resin held the ferrous iron with weak chemical bonds that broke quickly in the presence of a slightly acidic solution. The hydrogen ions generated during the galvanic reaction of ferric iron took part in the desorption of its ferrous state counterpart. So, an acceptable level of the iron galvanic desorption was reached (above 96 %, Table 8) only in the presence of 30 g/L hydrochloric acid. The main plus of galvanic iron desorption was the lower consumption of acid and an alkalisng agent at the next stage of rich-in-iron pregnant leach solutions processing. The galvanic desorption of

iron, however, was a strongly temperature-dependent process. For example, the process efficiency was lower than 60 % at room temperature, and the value of desorption reached almost 80 % at a temperature of 50 °C (Table 9). If only the temperature was maintained at 70 °C or higher, the efficiency of the galvanic iron elution was comparable to the efficiency determined with a desorption solution at a highly acidic pH. The galvanic iron elution was a time-dependent process. It resulted from the presence of a heterogeneous mixture consisting of three phases (gaseous, solid, and aqueous) and the relevant surface-controlled processes carried out in pairs between them. Because of the lower kinetic of the galvanic iron reduction, the rate-limiting process received the optimal value of iron desorption after 30 minutes of the process duration (Table 10). We obtained higher iron concentration in the desorption solution when galvanic iron reduction occurred at an A : R ratio lower than 2.5 : 1. However, it was needed to increase the process duration to an hour in that case (Table 11).

Conclusions

The ferrous iron oxidation to ferric state was a compulsory preliminary process that made possible the iron adsorption from acid mine drainage by ion exchange resin LEWATIT MonoPlus TP 207 to carry out with a higher rate and selectively at the value of 1.63 for equilibrium pH. The maximum amount of ferric iron adsorbed on the ion-exchange resin was 16.6 mg/g resin when the conditions at which the process took place were equilibrium pH 1.63, the temperature of 30 °C, aqueous: resin ratio (A : R) 5 : 1, and agitation time of 10 minutes. The optimal conditions for galvanic elution of ferric iron from the loaded ion-exchange resin LEWATIT MonoPlus TP 207 in the presence of H_2 and at A : R of 2.5 : 1 were 30 g HCl/L, the temperature of 70 °C, and duration of 30 minutes. This iron desorption method enabled the resin regeneration to be carried out with insignificant hydrochloric acid consumption.

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