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Biosorption of hexavalent chromium from aqueous solution onto pomegranate seeds: kinetic modeling studies

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Abstract Hexavalent chromium has been proved to be the reason of several health hazards. This study aimed at evaluating the application of pomegranate seeds powder for chromium adsorption (VI) from aqueous solution. Chromium adsorption percentage (VI) increased with increasing the adsorbent dosage. Chromium adsorption capacity (VI), at pH = 2 and 10 mg/L initial metal concentration, decreased from 3.313 to 1.6 mg/g through increasing dosage of adsorbent from 0.2 to 0.6 g/100 ml. The adsorption rate increased through increase in chromium initial concentration (VI). However, there was a removal percentage reduction of chromium (VI). Chromium adsorption kinetics by different models (pseudo-firstorder, modified pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion, Boyd kinetic) was investigated as well. Studies on adsorption kinetic indicated that the experimental data were matched by pseudo-secondorder model ($R^2 = 0.999$) better. Obtained results demonstrated the pomegranate seeds can be used as an

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effective biomaterial and biosorbent for hexavalent chromium adsorption from aqueous solutions.

Keywords Adsorption · Chromium · Water treatment · Pomegranate seeds

Introduction

The impurity and pollution of water resources made by heavy metals has become a substantial issue, toxicological importance consequence in ecosystem, agriculture and public health (Malkoc et al. 2006; Shadborestan et al. 2013). Chromium, together with its compounds, are vastly applied in a diversity of industrial applications, such as leather tanning, electroplating cement preserving, pigments paints, textile fabric and steel fabrication (Levankumar et al. 2009; Malkoc et al. 2006; Najim and Yassin 2009; Owlad et al. 2010). Among different toxic metals, chromium is of great concern. These industries produce a large volume of toxic sewage which are detached into the environment, results in solemn and serious problems and health risks for people (Dubey and Gopal 2007).Both Cr(III) and Cr(VI) are chromium permanent oxidation states (Najim and Yassin 2009). The Agency of Toxic Substances and Disease Registry (ATSDR) presented that Cr(VI) salt is in higher level of mobility compared to Cr(III); therefore, it is toxic (Owlad et al. 2010). Cr(VI) form is 500 times more toxic than what Cr(III) is. The International Agency for Research on Cancer (IARC) has classified Cr(VI) as a sort of I human carcinogen, while the US Environmental Protection Agency (US EPA) categorized it as an inhalation carcinogen (Levankumar et al. 2009). US EPA arranged Cr(VI) discharging limitation for surface water, below 0.05 mg/L (Park et al. 2007).



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Plenty of physical and chemical strategies are applied for removing Cr(VI) from water and wastewater, such as lime coagulation, electrochemical, solvent extraction, precipitation ultrafiltration, ion exchange, reverse osmosis and different biological processes (Di Natale et al. 2007; Dubey and Gopal 2007; Levankumar et al. 2009; Owlad et al. 2010). Mentioned processes contain inadequate efficiencies or may have some disadvantages, such as upside reagents and energy needs, toxic sludge production, which requires safe disposal, and high operational costs as well (Di Natale et al. 2007; Dubey and Gopal 2007; Levankumar et al. 2009). Development of a new eco-efficient and low-cost technology is required in which precious metals can be recovered through adapting the circular economy model and minimizing the metals' negative impact on whole environment. Using biomass for heavy metal adsorption from aqueous solutions is a kind of eco-friendly substitute due to group of positive features such as biomass availability in abundance, low cost of adsorbents, capability of treating large volumes of polluted water and wastewater at low operating cost, the possibility of recovering of the metal kinds and reuse and replication of biomass for numerous cycles after regeneration procedure. Adsorption is an economical and cost-effective method applied for the removing a wide variety of aquatic pollutants (Owlad et al. 2010). Various adsorbents were investigated to eliminate chromium from aqueous solutions. Natural materials available in large quantities or specified wastes made by agricultural activities are the most widely used classes of these absorbents. They illustrated unutilized resources which are widely available and environmentally friendly. Therefore, they are able to be used as low-cost adsorbents (Dubey and Gopal 2007).

A variety of agricultural waste products such as *Ocimum americanum* L. seed pods (Levankumar et al. 2009), sunflower waste biomass carbons (Jain et al. 2016), gooseberry seeds (Aravind et al. 2016), Acroptilon repens flower powder (Ghaneian et al. 2013) and maize tassel powder (Dehvari et al. 2013) have been investigated as normal biosorbents.

Pomegranate (*Punica granatum*), a kind of tiny and small tree with height of between five and eight meters, has been found in Iran, the Himalayas in northern India, China, USA and throughout the Mediterranean region. Regarding ability of this tree to adapt to harmful ecological conditions, it can grow in several regions throughout the country with arid and semiarid regions (Rahimi et al. 2012). It is one of the most precious fruits in Iran and is cultivated on a commercial scale. Pomegranate seeds which are by-products of pomegranate juice production are inexpensive as well (Ghaneian et al. 2015).

Studies have been carried out to remove pollutants by pomegranate seed and peel. The results of a study by Najim

and Yassin (2009) regarding removing chromium showed that the optimum pH values of Cr(VI) adsorption of modified pomegranate peel (MPGP) and formaldehyde modified pomegranate peel (FMPGP), respectively, were 2 and 3. Regarding the results, Cr adsorption onto MPGP and FMPGP followed the pseudo-second-order model (Najim and Yassin 2009). Ghaneian et al. (2015) applied pomegranate seed powder as a new biosorbent for removal of reactive red 198 dye. Outcome of their study demonstrated that an increase in adsorbent dosage and the retention time turned to increasing dye removal efficiency. An increase in initial dye concentration resulted a decreasing in the efficiency of dye removal. Rate of adsorption chivied a pseudo-second-order kinetic in these studies. Mentioned researches indicated that the biosorbent makes the effective removal of reactive red 198 enable (Ghaneian et al. 2015).

The principal purpose of current research was studying valorization of pomegranate seeds (a by-product of pomegranate juice production) for removing Cr(VI) from synthetic wastewater. Adsorbent (pomegranate seed powder) specified by scanning electron microscopy (SEM) to get an insight of the morphology of adsorbent. Batch adsorption experiments were applied for optimizing conditions and kinetic data fitted to different kinetic models to figure out the process. Present research was conducted in 2014, in the Environmental Chemistry Laboratory of the Environmental Health Engineering Department, Public Health school, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.

Instruments and methods

Materials

Applied materials were received through Merck Company. Cr(VI) solution prepared using $K_2Cr_2O_7$ analytical reagent degree. Distilled water has been applied to provide solutions. 1000 mg/L stock solution prepared through dissolving required amount of Cr(VI) salt in deionized water. Favorable concentrations of chromium solution were obtained by consecutive dilutions of the stock solution.

Chromium detection

According to the recommendations of the United States Environmental Protection Agency (USEPA), the admissible limits for Cr(VI) in discharges are, respectively, 0.1 and 0.05 mg/L in surface and portable water (Aravind et al. 2016). The Cr(VI) was computed using the colorimetric technique. The samples were acidified with phosphoric acid, compounded with a solution of 1.5 diphenyl carbazide (DIPC) in acetone, and finally investigated and analyzed by spectrophotometer at a maximum wavelength of 540 nm (AWWA 2005). The detection limits for Cr(VI) which were enriched into reagent water ranged from 0.0044 to 0.015 μ g/L (EPA 2015).

Preparation of biosorbent

To prepare adsorbent using pomegranate seed waste, pomegranate was obtained from a local farm in Yazd, Iran, location of the major pomegranate harvest in the region. The pomegranate seed powder was separated and rinsed with deionized water. After boiling in water for 2 h, the seeds were dried up at temperature between 100 and 105 °C in an air oven for 24 h, and this was followed by milling using a small electrical mill. The standard sieves with 40–100 mesh sizes were used to sieve the adsorbent. A glass bottle was used to store the adsorbent for further experimental use when needed.

Adsorption study

The adsorption studies were conducted at room temperature (25 \pm 2 °C). Batch adsorption researches were accomplished using 250 mL Erlenmeyer flasks with 100 mL of test solutions containing 2 and 10 mg/L Cr(VI) at a solution pH of 2, adsorbent dosage of 0.2-0.6 g/ 100 mL and at contact time of 15-180 min (adsorption equilibrium time was 120 min, data not shown). Removing process of Cr(VI) on pomegranate seed was examined at pHs 2, 3, 4 and 6. Regarding results obtained (results not shown), maximum removal at an initial pH of 2, all experiments conducted at pH 2. pH value is adjusted through 0.1 M H₂SO₄ or 0.1 M NaOH before addition of biomass. Flasks have been agitated on a shaker (150 rpm) for a predetermined contact time. Samples are filtered through 0.2-µm filters after equilibrium, and the final concentration of Cr(VI) determined in the filtrate using UV-Visible spectrophotometer (Optima SP-3000 Plus model, Japan) at 540 nm, according to standard methods.

The amount of adsorbed Cr(VI) per unit weight of pomegranate seeds powder at time *t*, q_e (mg/g), and percentage of Cr(VI) removal, *R* (%), were demonstrated by following equations:

$$q_{\rm e} = \frac{(C_0 - C_t)V}{M} \tag{1}$$

$$R = \frac{C_0 - C_t}{C_0} \times 100$$
 (2)

 C_0 and C_t are the primary Cr concentration (VI) and Cr concentration (VI) at time *t* in solution (mg/L). *V* means the volume of solution (L). *M* means the mass of the adsorbent (g) (Samarghandy et al. 2011).

Analysis of SEM

Surface morphology of the pomegranate seed powder before and after Cr(VI) adsorption was conducted through Scanning Electron Microscopy (SEM) KYKY-EM3200, operating at a 25 kV accelerating potential. To achieve this goal, a thin layer of pomegranate seed powder was deposited on conductive glue and coated with about 20 nm gold layer, before the SEM images were formed.

Results and discussion

Biosorbent characterization

Difference between surface of the pomegranate seed powder before and after Cr(VI) adsorption was studied using SEM. Figure 1a, b indicates the SEM images. Observations of the SEM displayed that there was a shift in adsorbent surface morphology after Cr(VI) adsorption, and it became rough after ions adhered to the biosorbent's surface. This suggests that Cr(VI) ions absorbed to the pores of the adsorbents, thus forming a layer of Cr(VI) on the surface of the adsorbent.

Effect of biosorbent dose

Figure 2a, b shows the comparative data regarding the impact of adsorbent dosage on the Cr removing (VI) through pomegranate seed powder at primary Cr(VI) concentrations of 2 and 10 mg/L. It is clear that the concentration of Cr(VI) adsorption was notably affected by the amount of adsorbent. Initially, there was a sharp reduction in Cr(VI) balance concentration by increasing the adsorbent dosage up to 0.4 g/L, but beyond this concentration, a decrease in Cr(VI) equilibrium concentration was negligible. It might be resulted by the decrease in concentration gradient. The maximum removal efficiency of Cr(VI) ion by pomegranate seed powder with a dose of 0.6 g/100 mL was found to be, respectively, 99.5 and 96.2% for concentrations of 2 and 10 mg/L hexavalent chromium. Increasing removal efficiency of Cr(VI) ions might ascribed to increasing the number of existing sites for adsorption (Aravindhan et al. 2012; Brungesh et al. 2015; Nharingo et al. 2016). Hereupon, the optimum adsorbent dosage for the utmost removal of Cr(VI) was obtained at 0.6 g/100 mL.

Distribution coefficient, K_d , describes the binding ability of adsorbent surface to the adsorbate. The K_d value can be calculated from the below formula:

$$K_{\rm d} = \frac{(C_0 - C_{\rm e})V}{C_{\rm e}m} \tag{3}$$





Fig. 1 SEM images of pomegranate seeds powder before adsorption (a) and after Cr(VI) adsorption (b)

Fig. 2 Effect of adsorbent dosage on adsorption of Cr(VI) on pomegranate seed powder adsorbent at initial Cr(VI) concentration: 2 mg/L (a) and initial Cr(VI) concentration: 10 mg/L (b) (time = 24 h, pH = 2)



 Table 1 Comparison of adsorption capacities of chromium with different adsorbents

Adsorbents	Adsorption capacity (mg/g)	References Oliveira et al. (2005)	
Raw rice bran	0.15		
Oak pine	0.47	Park et al. (2008)	
Rice husk carbon	1.581	El-Batouti et al. (2015)	
Almond green hull	2.04	Sahranavard et al. (2011)	
Pomegranate seeds	3.31	This study	
Almond shell	3.40	Pehlivan and Altun (2008)	
Modified wheat bran	4.53	Kaya et al. (2014)	
Acroptilon repens flower powder	5.72	Ghaneian et al. (2013)	

 C_0 and C_e (mg/L) are the primary and balanced concentration of Cr(VI) in solution, V (L) is Cr(VI) volume solution and m (g) is the mass of adsorbent. When adsorbent surface is alike, the K_d value remains the same with the adsorbent dosage, while if adsorbent surface is heterogeneous, the K_d value grows with the increase in adsorbent dose (Yu et al. 2013). From Fig. 2, there is an increase in K_d value with increase in the adsorbent dosage, which indicated that the surface of pomegranate seed powder was heterogeneous.

Considering obtained results, through increase in adsorbent dosage from 0.2 to 0.6 g/100 mL, adsorption capacity (q_e) decreased for 2 mg/L chromium, from 0.820 to 0.332 mg/g and for 10 mg/L chromium, from 3.31 to 1.6 mg/g. Ghaneian et al. (2015) studied the removal of reactive red 198 dye by pomegranate seed powder. An increase in adsorbent resulted to increase in the efficiency of dye removal from their study (Ghaneian et al. 2015). Aliabadi et al. (2012) reported same results as well (Aliabadi et al. 2012).

The chromium adsorption content obtained in current study was compared with some other researches and the results are shown in Table 1.

Considering results, chromium adsorption capacity by pomegranate seed was higher in some cases and lower in others.

Kinetic modeling

To asses and examine the adsorption kinetics of Cr(VI) by pomegranate seed powder, different kinetic models, specifically pseudo-first-order, pseudo-second-order, modified pseudo-first-order, Elovich, Weber & Morris and Boyd models, were used.

Pseudo-first-order kinetic model

Pseudo-first-order kinetic model has been applied in many studies, for the prediction of adsorption kinetics. Pseudofirst-order formula is dedicated below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

 $q_{\rm e}$ and q_t are Cr(VI) adsorbed on pomegranate seed powder (mg/g) at equilibrium and at time t (min), k_1 (g/mg min) means the rate constant of the pseudo-first-order sorption, which can be calculated by plotting log ($q_{\rm e} - q_t$) versus t (Yousef et al. 2011) (Fig. 3a).

Modified pseudo-first-order kinetic model

Pseudo-first-order model predicted capacities were not close to the obtained data from experimental and the observed deviation from the straight line at 15 min of contact shows that the whole range of kinetic data is not described by the pseudo-first-order kinetic. To clear this error, the improved pseudo-first-order model was recommended (Ofomaja et al. 2010).

The modified pseudo-first-order rate equation can be derived as below (Barkakati et al. 2010):

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln(q_e) - K_{1m}t$$
(5)

where q_e , q_t and t have the equal meaning as described in Eq. (4) and k_{1m} is the rate constant of the modified pseudo-first-order sorption. If the adsorption process obeys the improved pseudo-first-order model, a plot of $q_t/q_e + -\ln(q_e - q_t)$ against t should be a straight line (Barkakati et al. 2010; Zazouli et al. 2013). As it is observed in Fig. 3b, the deviations from the experimental data at 15 min in the modified pseudo-first-order model plot.

Pseudo-second-order kinetic model

The pseudo-second-order kinetic has been used for the analysis of chemisorption kinetics from liquid solutions, in which the linear type of the model presented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

 $q_{\rm e}$, q_t and t have the equal meaning as described in Eq. (4). k_2 (g/mg min) and h ($k_2q_{\rm e}^2$) are the rate constant of the





Fig. 3 a Pseudo-first-order, \mathbf{b} modified pseudo-first-order, \mathbf{c} pseudo-second-order and \mathbf{d} Elovich plots for Cr(VI) adsorption on pomegranate seed powder

pseudo-second-order sorption and the primary adsorption rate, respectively (Boparai et al. 2011; Taghavi et al. 2015). t/q_t layout versus t should give a straight line if the pseudosecond-order kinetics is appropriate, and q_e , k_2 and h can be specified through the plot slope and intercept (Kumar et al. 2011). The plots (Fig. 3c) found to be linear with good correlation coefficients (0.999 and 0.999 for 2 and 10 mg/L initial Cr(VI) concentration). Moreover, the theoretical $q_{e(cal)}$ values were in good agreement with the experimental $q_{e(exp)}$ values in the case of pseudo-second-order kinetics at two examined concentrations. This implies that the pseudosecond-order model agrees well with the experimental data (Kumar et al. 2010) and can be applied to the Cr(VI) adsorption on pomegranate seed powder. Therefore, ratelimiting step of Cr(VI) biosorption onto pomegranate seed powder maybe chemisorption. As observed in Table 1, the value of the rate constant k was found to reduce with increase in primary Cr(VI) concentration for the pomegranate seed powder. This may be ascribed to the minor competition for the sorption available surface sites at lower concentration. At higher initial concentrations, the competition for the available surface sites will be much higher, with a consequence of lower sorption rates (Kumar et al. 2011).

Elovich model

Elovich kinetic model has been widely applied to describe the adsorption of gas onto solids widely (Heimberg et al. 2001; Rudzinski and Panczyk 2000). It has also been used to explain the adsorption pattern of some pollutants from aqueous solutions (Zarrabi et al. 2015). This formula is one of the most effective kinetic models for explaining chemisorption (Jamshidi et al. 2013; Zarrabi et al. 2015). Elovich's model expressed as below (Kumar et al. 2011):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{7}$$

 α is the initial adsorption rate in (mg/g.min) and β (g/mg) is the desorption constant associated with the extent of the surface coverage and activation energy for chemisorption. The resulting plot is indicated in Fig. 3d. Parameters of kinetic calculated from various models are dedicated in Table 1.

Intraparticle diffusion model

There are three continuous mass transport stages, such as (1) diffusion of film, (2) intraparticle or pore diffusion and (3) sorption to interior sites regarding the adsorption of



pollutants from the solution, by an adsorbent. The third stage is quick, as film and pore diffusions are the basic steps that control rate of adsorption. The intraparticle diffusion model, on the basis of the theory proposed by Weber and Morris, was applied for further analysis of the kinetic data, to understand the diffusion mechanism (Barkakati et al. 2010). The below formula was proposed by Weber and Morris:

$$q_t = k_{\rm id} t^{1/2} + C \tag{8}$$

 $k_{\rm id}$ is the intraparticle diffusion rate constant (mg/g h^{1/2}), q_t and t are adsorbate quantity and contact time, and C means the intercept that give information according to the boundary layer thickness. Regarding equation, q_t plot versus $t^{1/2}$ must be a straight line with a slope k_{id} and intercept C, if the adsorption mechanism obeys the intraparticle diffusion process (El Nemr et al. 2015). The values of k_{id} were found to be 0.09 and 0.456 mg/g h^{1/2} at different primary Cr(VI) concentrations of 2 and 10 mg/L, respectively. Figure 4 indicates the adsorption process at two concentrations of Cr(VI) by pomegranate seed powder at a pH of 2. This plot intercept shows the boundary layer impact. The bigger intercept displays the larger contribution of the surface sorption in the rate controlling stage. Intraparticle diffusion is the single rate-limiting stage when the regression in the plot is linear and passes through the origin. The various extent of sorption in the initial and final stages of the process resulted in the dual nature of the curves that may be ascribed to the boundary layer diffusion and the impacts of intraparticle diffusion on sorption in the primary and later steps, respectively (Acharya et al. 2009). The plots of q_t versus $t^{(1/2)}$ are linear but do not pass through the origin that it can be regarding difference in the rate of mass transfer in the primary and final steps of adsorption (Kumar et al. 2011). This implies that the mechanism of Cr(VI) adsorption process using pomegranate seed powder is complex and both the surface adsorption and intraparticle diffusion contribute to the rate controlling step. Moreover, some degree of boundary layer control exists, and intraparticle diffusion is not the only rate-limiting step, but it is involved in the rate controlling step of sorption, or all steps are operating at the same time (Kumar et al. 2011).

Boyd model

Third step in the adsorption dynamics is considered insignificant it presumed to be very quick. Difference between absorptive molecules' film diffusion and particle diffusion is required for designing process (Kumar et al. 2011). Boyd's kinetic model for adsorption reaction is on the basis of diffusion via the boundary liquid film if adsorption kinetics will be considered a chemical



Fig. 4 Intraparticle diffusion model plot for Cr(VI) adsorption on pomegranate seed powder



Fig. 5 Boyd model plot for Cr(VI) adsorption on pomegranate seed powder

phenomenon (Barkakati et al. 2010). Boyd's kinetic equation in the adsorption process used to determine the slowest step. It is shown as below:

$$F = \frac{q_t}{q_e} \tag{9}$$

 q_e is the quantity of adsorbed Cr(VI) per unit mass adsorbent at balanced condition (mg/g) and q_t shows the quantity of adsorbed Cr(VI) per unit mass adsorbent in any time t (mg/g), F corresponds to the fraction of adsorbed metal at any time t and B_t is a mathematical function of F. simplified film diffusion model of Boyd can be as below:

$$B_t = -0.4977 - \ln(1 - F) \tag{10}$$

If B_t plot versus t is lineal, and crossing through the origin, pore diffusion is the slowest (rate controlling) stage in biosorption process; otherwise, diffusion of surface (film) will be the controlling stage (Acharya et al. 2009). As seen from Fig. 5, the plots are linear and will not across through



Table 2 Adsorption kinetic model rate constants for Cr(VI) adsorption on pomegranate seed powder at different concentration

Kinetic models		Initial Cr(VI) concentration	
		2 mg/L	10 mg/L
Pseudo-first-order	$q_{\rm e}$ (mg/g)	0.129	0.705
	<i>k</i> ₁ (1/min)	0.008	0.009
	R^2	0.843	0.953
Modified pseudo-first-order	$q_{\rm e} ({\rm mg/g})$	0.241	0.782
	k _{1m} (1/min)	0.006	0.007
	R^2	0.888	0.978
Pseudo-second-order	$q_{\rm e} ({\rm mg/g})$	0.320	1.56
	k_2 (g/mg min)	0.286	0.049
	R^2	0.999	0.999
Elovich	α (mg/g min)	0.048	0.237
	β (g/mg)	0.06	0.256
	R^2	0.887	0.965
Intraparticle diffusion	$K_{\rm P} \ ({\rm mg/g} \ {\rm h}^{0.5})$	0.456	0.090
	R^2	0.770	0.890

the origin. Therefore, it clears that film diffusion controls the biosorption process.

The correlation of the experimental data with the lineal shape of the six models was examined, and correlation coefficient R^2 and the derived rate constants based on the models of Cr(VI) kinetic biosorption are listed in Table 2.

Study of the experimental data along with the pseudosecond-order model indicated the best agreement of the data with an extremely high correlation coefficient. Moreover, chemical adsorption is a limiting stage that controls the biosorption process (Samarghandye and colleagues. 2011). The modified pseudo-first-order model is the second prominent kinetic pattern to create a competent fit to the test, followed by Elovich kinetic model, pseudofirst-order and lastly the intraparticle diffusion kinetic model.

Conclusion

In the current study, batch adsorption experiments for the adsorption of Cr(VI) ions from aqueous solutions were conducted using pomegranate seed powder as biosorbent. Based on the results, the Cr(VI) biosorption increased with increase in adsorbent dose. Adsorption capacity of Cr(VI) ions by pomegranate seed powder increased with increasing initial Cr(VI) ion concentration, but the removal percentage of Cr(VI) ions decreased. It was concluded that the Cr(VI) biosorption process on pomegranate seed powder is

chemisorption and the process follows pseudo-secondorder kinetic.

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