Application Of The Peanut Shell Biomass (Arachys Hypogaea) By The Elimination Of Chromium (VI) In Aqueous Solution

Heidi Martínez Aguilar
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
heidimtz12s@gmail.com

Sara A. Palomo Mora
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
saraki2801icloud.com

Atzin B. Jiménez Martínez
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
atzinj01@gamil.com

Juan F. Cárdenas González
Unidad Académica Multidisciplinaria Zona Media
Universidad Autónoma de San Luis Potosí. Río Verde, San Luis Potosí, México
jfkardenas_08@hotmail.com

Adriana S. Rodríguez Pérez
Unidad Académica Multidisciplinaria Zona Media
Universidad Autónoma de San Luis Potosí. Río Verde, San Luis Potosí, México
asarai28@hotmail.com

Ismael Acosta Rodríguez
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí
San Luis Potosí, México
iacosta@uaslp.mx

***Abstract*—The peanut is an oilseed native to South America that arrived in Mexico during pre-Hispanic times. It was discovered by the Spanish in a market in the great city of Tenochtitlan, who then took it to Europe and Africa, allowing its cultivation and consumption to spread throughout the world. Thanks to its magnesium, folic acid, fiber, copper, vitamin E, and arginine content, peanut consumption benefits the central nervous system, helps prevent heart disease, aids in weight loss, and improves skin health. For all these reasons, its consumption is recommended for pregnant women. Among its uses, it is primarily used in the preparation of foods such as cookies, breads, candies, cereals, and salads. In industry, it is used to manufacture butter, oils, flours, inks, moisturizers, and lip balms, and the peanut shells are a waste product that is reused as fuel for boilers, although their use is somewhat difficult because they produce a lot of smoke and ash. They are partially used as feed for livestock, especially pigs. Although the peanut shells have no protein value and are indigestible, they help to balance the nutrients in the other types of feed with which they are mixed. Too, serve as a substrate for poultry and as a growing medium for fungi. They are also associated with uses similar to those of wood shavings.**

On the other hand, hundreds of thousands of tons of peanut shells are disposed of annually globally, with estimates suggesting nearly half a million tons from households and factories alone, although the exact figures vary by region and year, with countries like the United States generating large quantities that require handling, often transformed into compost, animal feed or biofuel.

Therefore, the development of novel processes for converting these by-products into value-added products could provide a viable way to manage this waste problem and try to use them in activities that benefit the world, for example, their use as biosorbents for the removal of hazardous and/or toxic contaminants from different contaminated sites. Therefore, the objective of this work was to determine the removal capacity of Cr (VI) by the peanut shells biomass, finding a complete metal removal (100 mg/L) was achieved after 5 hours of incubation at pH 1.0, 28°C, 5 g of biomass, and 100 rpm. Furthermore, metal removal increased with higher incubation temperatures; at 60°C, 100% of the metal was removed after 75 minutes. The metal concentration did not significantly influence its removal at either 28°C or 60°C, although the highest removal percentages were observed at 200 mg/L. Increasing the bioadsorbent concentration also increased metal removal; with 10 g of biomass, 100% removal was observed after 2 hours of incubation. Finally, with 10 g of biomass, 89% and 93% of the metal present in naturally contaminated soil (200 mg/g) and water (200 mg/L) are eliminated.

Keywords—Peanut, Wastewater, Contamination, Chromium (VI), Removal

I. INTRODUCTION

Arachis hypogaea, commonly known as peanut, groundnut, or groundnut (from the Nahuatl word tlalcacahuatl), is a plant in the Fabaceae (or Leguminosae) family, commonly known as the legume family. Like most other legumes, peanuts harbor nitrogen-fixing bacteria in their root nodules, which improve soil fertility, making them valuable in crop rotations. Peanuts are contained in underground pods. [1]. They are widely cultivated in the tropics and subtropics by both small and large commercial producers; they are grown both as a grain legume and as an oil crop. Their geocarpy is atypical among legumes, which led the botanist Carl Linnaeus to name the species hypogaea, meaning 'underground'. Despite not meeting the botanical definition of a nut as “a fruit whose ovary wall hardens at maturity”, peanuts are generally categorized as nuts for culinary purposes [2]. Some people are allergic to peanuts and can have a potentially fatal reaction; this is distinct from allergies to other tree nuts. Peanuts are cultivated for their edible seeds, which are similar in flavor and nutritional profile to nuts such as walnuts and almonds, and, as a nut-like culinary nut, they are often served in similar ways in the cuisines of many countries [1].

This fruit is used to make foods such as peanut butter or cream, and its oil is extracted, which is widely used in the cuisine of India and Southeast Asia [1]. It can be consumed as a snack (usually toasted and salted or with added chili powder to give it a spicy flavor) or as part of cakes and sweets (usually as a decoration on donuts or as a topping for ice cream) [2]. Too, It contains amides, sugars, choline, arachin, oil (oleic, palmitic, stearic, arachidic, myristic and lignoceric acids, as components), proteins, and betaine [3], and is nutritious, blood-thinning, and cholesterol-lowering. The flour is used in products for diabetics (cookies, nougat), and the fruit is also used. It is harvested in September. Some people should avoid it, because this fruit is allergenic and also contains fiber. If proper handling practices are not followed, too, may contain high levels of aflatoxin, a mycotoxin produced by some fungi that can be dangerous to health [3]. There is also a possibility that (since is a legume eaten raw), and their lectins could cause atherosclerosis. However, it is also suggested that it may improve the lipid profile. Since there is no clear evidence in either direction, it is recommended not to overindulge in peanuts [3].

Furthermore, despite being high in calories, multiple studies conclude that both peanuts and nuts are beneficial for losing body fat and achieving or maintaining a healthy body composition, thus preventing obesity. A diet that includes peanuts has also been associated with a lower risk of cardiovascular disease, which in turn is associated with a lower risk of age-related cognitive decline. The protective effect against cognitive decline and Alzheimer's disease may also be related to resveratrol, of which peanuts are a significant source, thanks to its antioxidant effect [1].

On the other hand, during their processing, considerable quantities of shells, potentially polluting byproducts, are generated. However, after reuse, the shells are employed as animal feed and fertilizer. Significant quantities of peanut dust, shells, hulls, and stems, are also classified as agricultural waste. Since the vast majority of studies focus on oil and kernel production, peanut byproducts such as shells receive little attention [4]. Moreover, peanut skins are beneficial as they are rich in antioxidants, catechin, epicatechin, resveratrol, and anthocyanidins [5]. They may reduce the rate of free-radical-induced oxidation processes [5]. Antioxidants are able to neutralize and build stable compounds by donating additional hydrogen electrons to free radicals [5]. Previous research demonstrated that long-term consumption of peanut skin extract rich in plant polyphenols protects against cancer, cardiovascular disease, diabetes, osteoporosis, and neurological disorders [6]. Peanut skin also contains cellulose (40.5%), lignin (26.4%), and hemicellulose (14.7%) [7].

Too, the humanity has existed on earth for 200,000 years, and thanks to advances in medicine and technology, the quality of life has improved, leading to greater longevity. For example, in Mexico, between 1930 and 1990, life expectancy increased by 37 years, and it continues to rise gradually over time. However, the rapid growth of the world's population has required a surge in resource use, and in the rush to respond immediately, the impact on the environment has been neglected, resulting in considerable, even irreversible, negative effects, such as the depletion of non-renewable resources and the generation of harmful gases [8]. The environment includes the soil, rivers, lakes, seas, oceans, forests, jungles, mountains, and everything around humans and other living beings; as people's lives become simpler, everything created, invented, or discovered by humans must now also be included, as it forms part of the environment, making its control and regulation vital, and recognizing the point of equilibrium where the least or no degree of pollution is caused is of utmost importance [8]. Mexico, like other developing and developed countries, faces environmental problems that directly affect the nation's sustainability. These problems extend beyond the environmental sphere, impacting social and economic aspects as well. The main points to consider are the ways in which human activity causes damage. Forecasts showing the negative consequences of continuing to ignore these issues and failing to change the habits and behaviors that ultimately affect the planet have already been developed and have served as a basis for planning solutions [8], especially to remediate and/or eliminate environmental pollutants, such as heavy metals [9].

On the other hand, pollution is a simple consequence of the existence and development of living beings. It has existed since prehistoric times. Early human communities produced pollution, for example, through campfires, while the great civilizations of antiquity generated pollution through metals, but this did not pose a significant risk to the planet itself due to its localized nature. It remained relatively stable for a long time, but began to become a problem with the First Industrial Revolution in the mid-18th century, primarily in England, and has been steadily increasing ever since [9,10], and the pollutants are "those substances found in the natural environment that cause harmful effects on the environment itself and on the health of the living beings that inhabit it," therefore, their quantity is vast and they can be found practically everywhere, even where there is no human activity [10]. The heavy metals, belong to a set of chemical elements, which are found naturally in the earth's crust, possess stability, however, after human manipulation they become a source of degradation for any ecosystem, by affecting its regular course of action, among them are Arsenic, Cadmium, Chromium, Mercury and Lead [11].

The chromium (VI), in its polluting form, it is known as Chromium-6 or Cr-VI. It is odorless and tasteless and can be found naturally in rocks, soil, and plants. It can originate from industrial sources, finding its way into drinking water systems due to erosion and leaks. This element has the ability to form chemical compounds and has been used in numerous applications, including tanning, the production of catalysts, pigments, anti-corrosives, alloys, batteries, fungicides, and metal coatings, among many others [9]. Among the conditions it can cause in humans are liver damage, reproductive problems, respiratory tract problems, cough, wheezing, septal perforations and ulcerations, bronchitis, pulmonary dysfunction, pneumonia, in addition to being carcinogenic, mainly causing lung cancer [12]. Therefore, different investigations have been carried out for the implementation of different efficient, economical and beneficial methods for the elimination of this and other heavy metals from contaminated waters.

In Mexico, agribusiness is one of the most important activities due to its growth in recent years, and it is the one that generates the most by-products that are not used [13], among which are: coffee bagasse, agave, maguey, sugar cane, straws from different crops, organic residues of fruits and vegetables [14]. In this regard, the use of different plant products with the ability to accumulate and/or bioadsorb heavy metals has been reported, which include peanut shell biomass (*Arachys hypogaea*) for example: the removal of copper and fluorides [15], cadmium [16], and aqueous chemical waste[17], the removal of volatile organic compounds, and heavy metals [18], elimination of emerging pollutants [19], the removal of copper and nickel ions [20], and the biosorption of divalent metals [21], because of the above, the objective of this work was to determine the removal capacity of Chromium (VI) by peanut shell biomass (*A. hypogaea*).

II. EXPERIMENTAL

A. Biosorbent used

The *A. hypogaea* shell biomass, was obtained from the marketplace Republic, in the month of december of 2024, of the capital city of San Luis Potosí, S.L.P., México. To obtain the biomass, the shell was washed with EDTA 10% (p/v) for 24 hours, and after with trideionized water during 7 days at constant stirring, with water changes every 12 hours. Subsequently, it was boiling 1 hour to removal traces of the color and dust, and were dry at 80°C for 72 hours in an oven, ground in blender and stored in amber vials until use.

B. Biosorption studies and determination of hexavalent chromium.

For these studies, was used 5 g of dried biomass mixed with 100 mL of trideionized water containing 100 mg/L of the metal, in an Erlenmeyer flask at the desired temperature and pH. The flasks were agitated on a shaking bath Yamato BT-25 model. Samples of 5 mL were taken at different times, and centrifuged at 3000 rpm for 5 min. The supernatant liquid was separated and analyzed for chromium ions. Hexavalent chromium was quantifying by a spectrophotometric method with Diphenylcarbazide [22]. The information shown in the results section are the mean from three experiments carried out by triplicate.

III. RESULTS AND DISCUSSION

A. Effect of incubation time and pH

In this work, it was found that 5 g of the analyzed biomass removes 100 mg/L of the metal after 5 hours of incubation, pH 1.0, 28°C and 100 rpm, while at pH levels of 2.0, 3.0 and 4.0, the removal is less, although still very efficient (see Fig. 1).

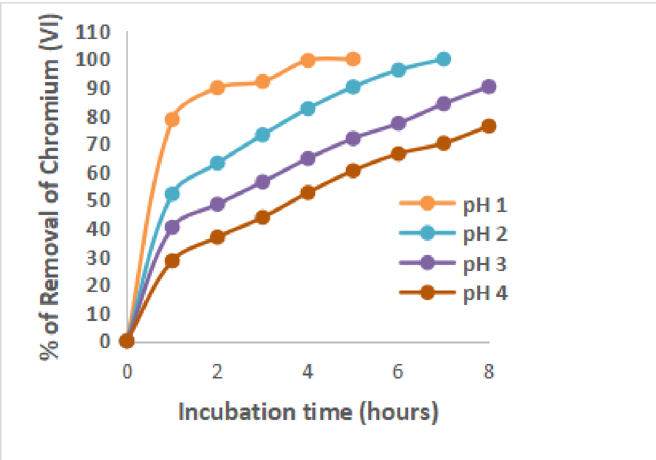

Figure 1. Effect of incubation time and pH on Chromium (VI) removal by peanut shell biomass. 100 mg/L Cr (VI), 100 rpm, 28°C. 5.0 g of biomass.

These results are different to what was reported 150 minutes with different natural biomasses [23], 120 minutes for *Moringa stenopetala* seed powder [24], 24 hours for the biomass of palm leaf-derived biochar [25], 30 minutes for in natura and magnetic nanomodified hydroponic lettuce roots [26]. Changes in the cell permeability of unknown origin, could partly explain the differences founded in the incubation time, providing greater or lesser exposure of the functional groups of the cell wall of the biomass analyzed [10]. Adsorption efficiency of chromium (VI) was observing a maximum at pH 1.0 and 7 hours with the biomass analyzed. The results showed with respect to the increase in pH resulted in decrease in the removal of the metal. It was reported an optimum pH 1.5 for adsorbents from agricultural waste material [26], a pH of 1.0 for in natura and magnetic nanomodified hydroponic lettuce roots [27]. Although other authors, report an optimum pH 3.0 for adsorbents from agricultural waste material [27], pH of 2.0 for dry raw biomasses of *Dioscorea rotundata, Elaeis guineensis, Manihot esculenta, Theobroma cacao* and *Zea mays* [23], a pH value of 2.0 and 4.0, for the removal of chromium (VI) from wastewater using *M. stenopetala* seed powder and banana peel powder [24], too, a pH value of 2.0 using palm leaf-derived biochar, tea stalk biochar, and waste of *Musa acuminata* residue [28, 29]. This was due to the dominant species (CrO_4^{2-} and $Cr_2O_7^{2-}$) of Chromate ions in solution, which were expected to interact more strongly with the ligands carrying positive charges [30].

B. Effect of temperature

Furthermore, if the incubation temperature is increased, the removal of the metal also increases, since at 60°C, 100% of the metal is removed in 75 minutes (Figure 2).

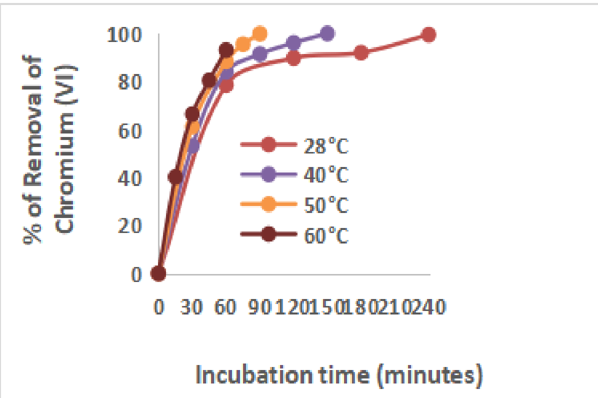

Figure 2. Effect of incubation temperature on Chromium (VI) removal by peanut shell biomass. 100 mg/L Cr (VI), 100 rpm, . 5.0 g of biomass.

Our results are coincident for the biomass of palm leaf-derived biochar, with the same temperature of incubation [28], by a reusable chitosan-modified multi-walled carbon nanotube composite [31], by dried twigs of *Melaleuca diosmifolia* [32], for the removal of the same heavy metal. But, they are different for removal of chromium (VI) from wastewater using *M. stenopeta* seed powder and banana peel powder, if increase this parameter, decrease the removal capacity of this biomasses [23], and for different natural biomasses, which exhibit higher adsorption efficiency at intermediate and low temperature values [25]. The increase in temperature increases the rate of removal of Cr (VI) and decrease the contact time required for complete removal of the metal, to increase the redox reaction rate [33].

C. Effect of initial metal concentration

Furthermore, at 28°C, the concentration of the metal does not significantly influence its removal, although at 200 mg/L, the best removal percentages are observed, while to 60°C, the total removal of the heavy metal was to 200 mg/L in 120 minutes, and at the other concentrations analysed, the removal was between 300 and 360 minutes (Figures 3 and 4).

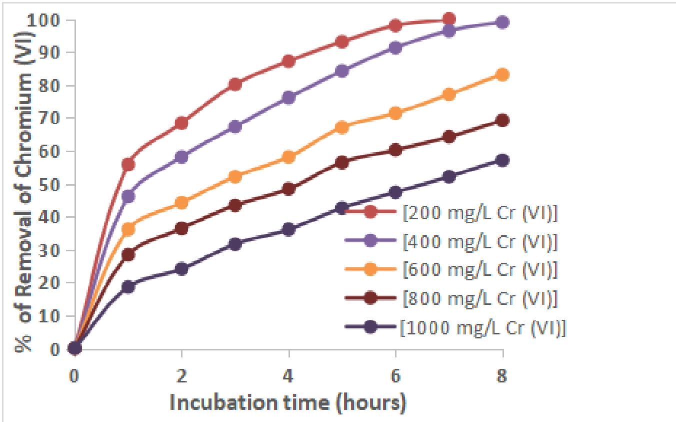

Figure 3.- Effect of initial metal concentration on Chromium (VI) removal by 5 g of peanut shell biomass biomass. pH 1.0, 28°C. 100 rpm.

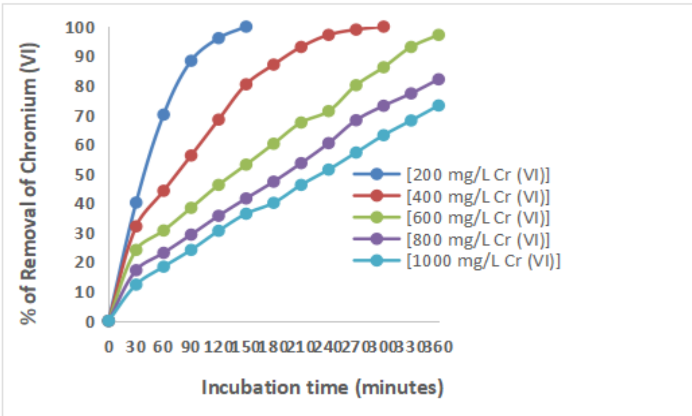

Figure 4.- Effect of initial metal concentration on Chromium (VI) removal by 5 g of peanut shell biomass. pH 1.0, 60°C. 100 rpm.

These results are coincident for the removal of this metal by *Cucumis sativus* biomasses [31], but are different for the chromium removal using *M. stenopetala* seed powder and banana peel powder, in which if increase the heavy metal concentration decrease the efficiency of removal and palm leaf-derived biochar [24, 28]. The increase in initial concentration of Chromium (VI), results in a decreased in the percentage of removal of the metal. This was due to the increase in the number of ions competing for the available functional groups on the surface of biomass [30, 31].

D Effect of biosorbent dose

In the figure 5, we depict the influence of biomass concentration on the removal capacity of Cr (VI). If we increase the amount of biomass, the removal of the heavy metal in solution increases significantly, because with 10 g of the natural biomass, 100% of the metal is removed after 3 hours of incubation, while with 5 and 1 g of the biomass, the removal is total after 4, and 8 hours, respectively, although it has been reported what with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption [34].

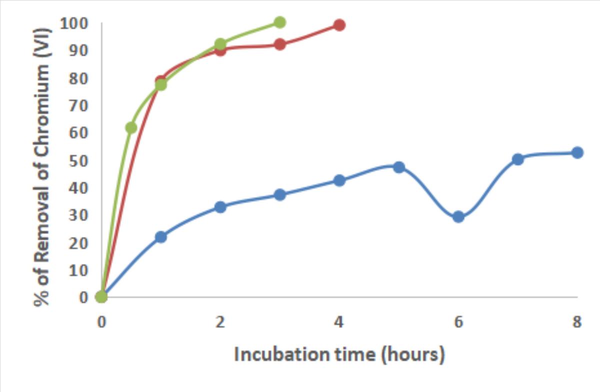

Figure 5. Effect of biomass concentration of peanut shell biomass, on the removal of 100 mg/L Cr (VI), 28°C, pH 1.0, 100 rpm.
1 g   5 g   10 g

These results are similar for the removal of chromium (VI) from wastewater using *M. stenopetala* seed powder and banana peel powder, if increase the biomass concentration of 5 to 20 g/L [23], for palm leaf-derived biochar [30], and *B. Cucumis sativus* biomasses [36]. Too, was reported a efficient removal of the metal if the biomass concentration was increased using modified Russian knapweed flower powder to initial concentrations of the heavy metal of 2, 10, and 15 mg/L with pH 2.0 [37].

E. Removal of Cr (VI) in industrial wastes with peanut shell biomass.

We adapted a water-phase bioremediation assay to explore possible usefulness of this biomass for eliminating chromium (VI) from industrial wastes. The biomass (10 g), was incubate with 10 g of non-sterilized contaminated earth with 200 mg/g, suspended in trideionized water to a final volume of 200 mL, and 200 mL of wastewater containing 200 mg/L of the same heavy metal (adjusted). It was observing that in 7 days of incubation, the chromium (VI) concentration of earth and water samples decrease between 85% and 90% completely in both samples (Figure 6), and the decrease level occurred without change significant in total chromium content during the experiments (date not shown). In the experiment carried out without biomass, the Chromium (VI) concentration of the earth samples decreased by about of 13% (date not shown); this might be caused by indigenous microflora and (or) reducing components present in the soil [10].

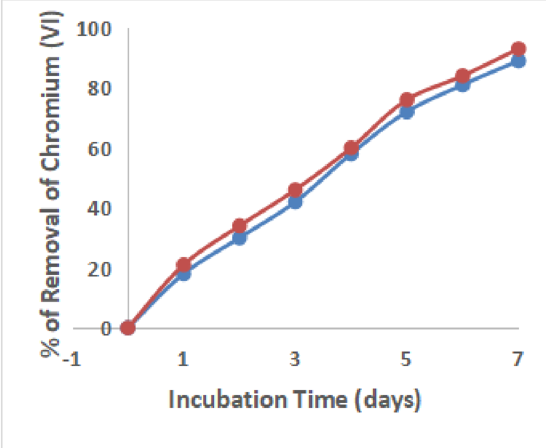

Figure 6. Removal of Cr (VI) in industrial wastes incubated with 10 g of peanut shell biomass. 28°C, 100 rpm, 10 g of contaminated earth with 200 mg/g and 200 mL of contaminated water with 200 mg/L.
Earth   Wastewater

These results coincide with the literature reports for another natural biomass, such as for different natural biomasses [24, 25, and 35], for *Ginkgo biloba* leaves can effectively remove soil Chromium (VI) and reduce Chromium (VI) to Chromium (III) via quercetin in soil (38), the removal of Chromium (VI) from wastewater using *M. stenopetala* seed powder and banana peel powder [24], for the biomass of palm leaf-derived biochar [28], the removal of chromium was found 95% from dilute tannery wastewater and 72% of chromium was eliminate directly from raw tannery effluents by using different quantities of *Nicotiana tabacum* biomass (38), for the phytoremediation of chromium-polluted waters in cold region [40], for waste of *M. acuminata* residue [29], and is more efficient that *Avena sativa* L. biomass, in which a lower uptake of chromium from soil in the Cr(VI)-contaminated, was observed [40].

IV CONCLUSIONS

The biomass analyzed, showed complete capacity of biosorption of 1000 mg/L of Cr (VI) in solution at different time of incubation, at 28°C adn 60°C, 100 rpm with 5 g of natural biomass, besides this natural biomass, efficiently removal the metal *in situ* (7 days of incubation, with 10 g of biomass), in both, earth and water contaminated, respectively. These results suggest their potential applicability for the remediation of this metal from polluted soils in the fields.

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