DOI:10.24996/ijs.2018.59.3B.1

ISSN: 0067-2904

Effect of Discharged Industrial Water from Tannery Plants in Nahrawan on Groundwater and Brick Quarries Soil

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Abstract

The discharged water from tannery plants is main source for pollution of soil and groundwater, especially in Nahrawan area. Water samples is collected from 10 sites of wells, discharged water and from using water in different levels of tannery and 7 soil samples from different sites inside factories area and outside it. The results shown that pH for samples of wells and discharged water were within allowable limits between 6.5- 8.5, except the value of pH recorded in the discharged water sample (after the addition of calcium hydroxide) was 12.8, as well as reached the highest value of total dissolved salts (TDS) 7800 ppm in same samples. It also reached its highest value of electrical conductivity (EC) 8200 µS/cm. The results showed that most samples of discharged water recorded high values of turbidity reached to 557 NTU, while the lowest values recorded in water wells and water sample of Nahrawan village. The samples of discharged water was contained high concentration of relatively heavy elements (Pb and Ni), while not sensing concentration of (Cd and Cr), especially for non-use of chromium in the tanning process because of the lack of economic viability by the owners of the factories. The results of analysis of heavy elements in the soil samples to the concentration of Pb in the samples were all within the limits of Iraqi standard was 50-300 ppm. The results indicated that the highest concentration of Ni recorded in samples of soil in the east and south-eastern tanneries exceeding the Iraqi standard concentration of Ni in the soil the amount of 30-75 ppm, while the concentration of Ni in other soil samples was within the limits of the Iraqi standard, while not sensing by concentration of (Cd and Cr) in these samples.

Keywords: Tannery factories, Industrial water, Heavy metals.

تأثير المياه الصناعية المصرفة من معامل الدباغة في النهروان على المياه الجوفية وتربة مقالع الطابوق

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الخلاصة

تعتبر المياه المصرفة من معامل الدباغة مصدرا مهما لتلوث التربة والمياه الجوفية، خاصة في منطقة النهروان. تم الحصول على 10 نماذج من مياه الآبار والمياه المصرفة في مراحل الدباغة المختلفة، كذلك تم الحصول على 7 نماذج تربة من مواقع مختلفة داخل منطقة المعامل ومن تربة مقالع الطابوق التي تستخدم في صناعة الطابوق. أشارت نتائج فحوصات نماذج المياه إلى إن قيمة الأس الهيدروجيني (pH) لأغلب نماذج

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مياه الآبار والمياه المصرفة كانت ضمن الحدود المسموحة 6.0-8.5 باستثناء نموذج الماء المصرف (بعد إضافة النورة) الذي بلغت قيمته 12.8. كذلك بلغ أعلى تركيز للأملاح الذائبة الكلية (TDS) (7800 جزء بالمليون) في النموذج نفسه. كما سجلت أعلى قيمة التوصيلية الكهربائية (EC)(8200 مايكروسيمز/ سم). أظهرت النتائج إن أغلب نماذج المياه المصرفة سجلت قيم عالية للعكورة وصلت الى NTU 557، بينما سجلت أدنى قيمها في مياه الآبار ونموذج ماء قرية النهروان. احتوت نماذج المياه المصرفة تراكيز عالية نسبيا من العناصر الثقيلة (الرصاص والنيكل)، بينما لم يتم التحسس بتراكيز الكادميوم والكروم في هذه النماذج، لعدم استخدام الكروم في عملية الدباغة بسبب عدم جدواها الاقتصادية من قبل أصحاب المعامل. أظهرت نتائج تحليل العناصر الثقيلة في نماذج التربة أن تركيز الرصاص في النماذج جميعها كانت ضمن الحدود المسموح بها البالغة (50-300 جزء بالمليون). كما أشارت النتائج إلى إن أعلى تركيز للنيكل سجل في نماذج التربة الواقعة شرق وجنوب شرق معامل الدباغة متجاوزا المواصفة العراقية لتركيز النيكل في التربة البالغة (30-75 جزء بالمليون)، بينما كان تركيز النيكل في نماذج الترب الأخرى ضمن المواصفة العراقية، بينما لم يتم التحسس بتركيز الكادميوم والكروم في تلك النماذج.

Introduction

Environmental pollution is one of the major problems of the world and it is increasing day to day due to urbanization and industrialization [1]. Tannery waste is generated in huge amounts during the process of tanning by leather industries throughout the world. It has been considered one of the most polluted industrial wastes and contains high amounts of metals which are very toxic to plants, animals and soil. Tannery wastes are of serious consequence since it has a role in pollution of fresh water bodies, streams and land [2]. The contamination of soils with heavy metals or micronutrients in phototoxic concentrations generates adverse effects not only on plants, but also poses risks to human health [3]. The industrial water discharge is one of the main sources of water pollution. There are some industries, disposal of water in large quantities, such as cooling water, solvents, chemicals used in production processes and others to water resources, either directly into rivers, lakes and other water bodies or indirectly through disposal in sewage systems, and then disposed to water sources after treatment [4].The pollutants resulting from the tanning processes involved in the wastewater is divided into two categories: organic contaminants such as proteins, fats, grease, dyes and inorganic contaminants such as salts, phosphate, nitrate, sulfate, chromium (Cr) [5]. In the environment, heavy metals are toxic and resist to bio-degradation which are discharging pollutants from industrial wastewater. Disposal of effluents from the industries has resulted in serious contamination of numerous sites. Numerous metals such as Pb (lead), Cr (chromium), Cu (copper), Zn (zink), Cd (cadmium)…etc. have toxic effects on human's health and also non-renewable resources [6]. Chronic Pb poisoning leads to inflammation of the kidneys and their damage. Exposure and chronic Pb poisoning lead to peripheral nerve paralysis, especially the motor nerve, and affect nerve cells in the spinal cord to inflammation and the occurrence of serious infections in the brain-encased tissue or nerve cells itself [7]. Cd poisoning leads to kidney damage, high blood pressure and replacement of calcium in the bones. Ni (Nickel) is a relatively toxic element, but its high doses lead to health effects, including dermatitis, its effect on the kidneys, the occurrence of rotor and dyspnea, and can cause cancer especially nickel compounds such as nickel sulphide [8]. Industrial wastewater from tanning plants is disposed in the form of liquid and solid products, through the use of water and various chemicals during the stages of tanning operations. During the stages of tanning operations, normal water (well water) is used to wash the skin of manure and salt (NaCl), and addition of sodium hypochloride or food salt. In the phase of removing hair or wool, uses sodium sulphide (Na_2S) and add calcium hydroxide ($Ca(OH)_2$). During removable, ammonia sulphate, hydrochloric acid and the commercialized bazine (eurobon) are added. In the acidification phase, NaCl and sulfuric acid (H_2SO_4) are added [9]. At present, tanning by chromium is not carried out, because of its economic inefficiency and the owners of the factories export their leather products outside Iraq after the completion of the process. There are many researches included discharged industrial wastewater from tannery on groundwater, soil and human health. Alvarez-Bernal et al, [10] studied effects of tanneries wastewater on chemical and biological soil characteristics in the town of Leon, Guanajuato, Mexico, almost 25 years of irrigation of agricultural land with water from the river Turbio. The results shown that significantly increased the electrical conductivity (EC) from 0.64 to 2.29 dS m^{-1}. Irrigation with water from the river Turbio, total concentration of Cr four-times and Cu two-times in the clayey soils. Agrawal. et al, studied of heavy and transition elements in tannery effluents and its impact on soil around Kanpur, India, were conducted in summer season of 2015 in (8) locations of tannery affected area of (Jajmau, Kanpur) and it deals with the assessment of pollution due to toxic heavy metals in the industrial waste water effluents collected from (Jajmau, Kanpur). The concentration level of magnesium, phosphate, nitrate, fluoride, phenol, oil and grease were above the permissible limit. The metals like Cd, Cr, Cu, Ni, Pb and Zn were found in significant quantities. We found the soils are highly contaminated due to tannery activity at (Jajmau, Kanpur). Afzal, et al, [11] assessed the heavy metal contamination of soil and groundwater at the leather industrial area of (Kasur, Pakistan). Soil and groundwater samples were collected from the study area and analyzed for Cr, Ni, Cd, Pb, Zn, Co (cobalt), by atomic absorption spectrophotometric method. The data revealed that soil and groundwater in the study area are highly contaminated with all tested heavy metals. In particular, Cr concentrations varied from 1970 to 2980 mg kg^{-1} and 0.82 to 2.25 mg L^{-1} in soil and groundwater, respectively.

The aims of current research are study the effect of untreated industrial water discharged from tanning plants in the Nahrawan area on groundwater and soil used in the manufacturing of bricks in the Nahrawan laboratories near the tanning plants. Also, determine concentration of some heavy elements in water and soil models, as well as determine the physical and chemical properties in industrial water models and well water in the tanning plant area.

Study Area

Nahrawan area lies about (35 km) east of Baghdad. The tanning and brick factories are a large number of industrial establishments located in the study area. There are (43) tanning plants, which have been established since 1990 and are exploited by the private sector and about (100 brick factories) established since 1985, used by private sector, and located northeast tanning plants area. The study area is located in the eastern part of the Mesopotamian Plain, which stretches from Samarra to the Arabian Gulf to the south [12]. (Figure-1) represents the study area showing industrial, groundwater and soil samples. (Figure -2) showed discharged industrial water from tannery plants and groundwater in brick quarries.

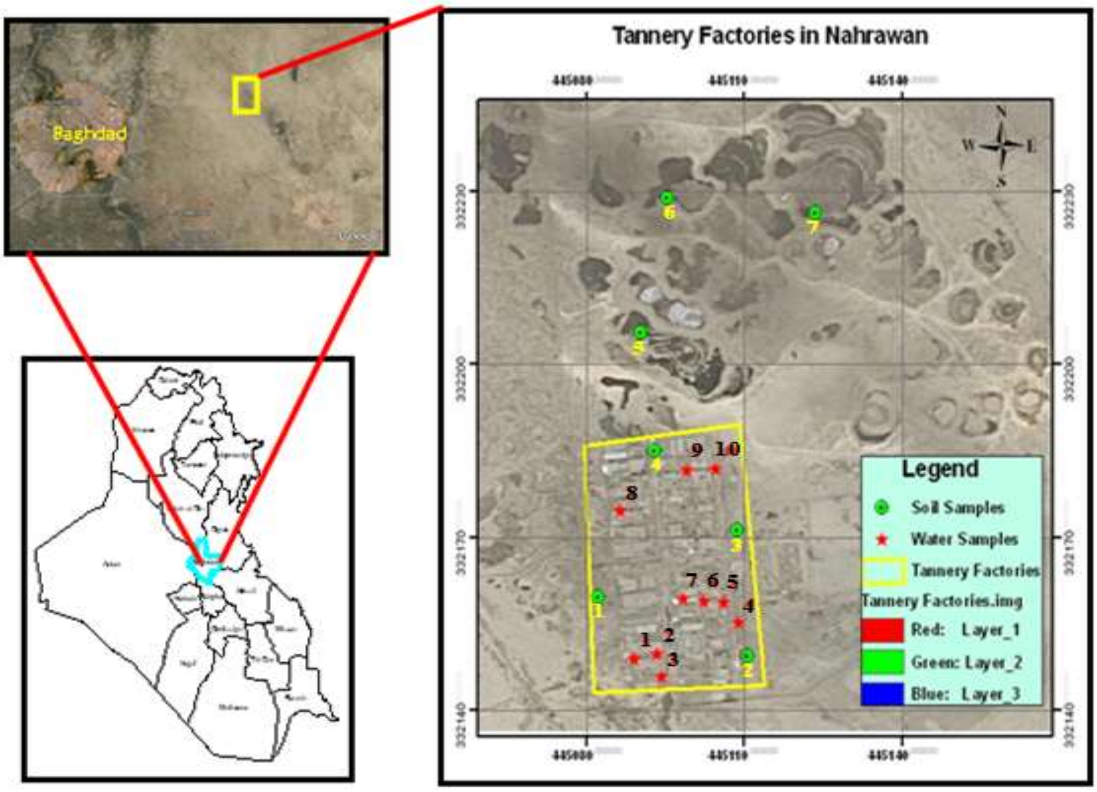


Figure 1- Sites of Industrial, groundwater and soil samples in Nahrawan

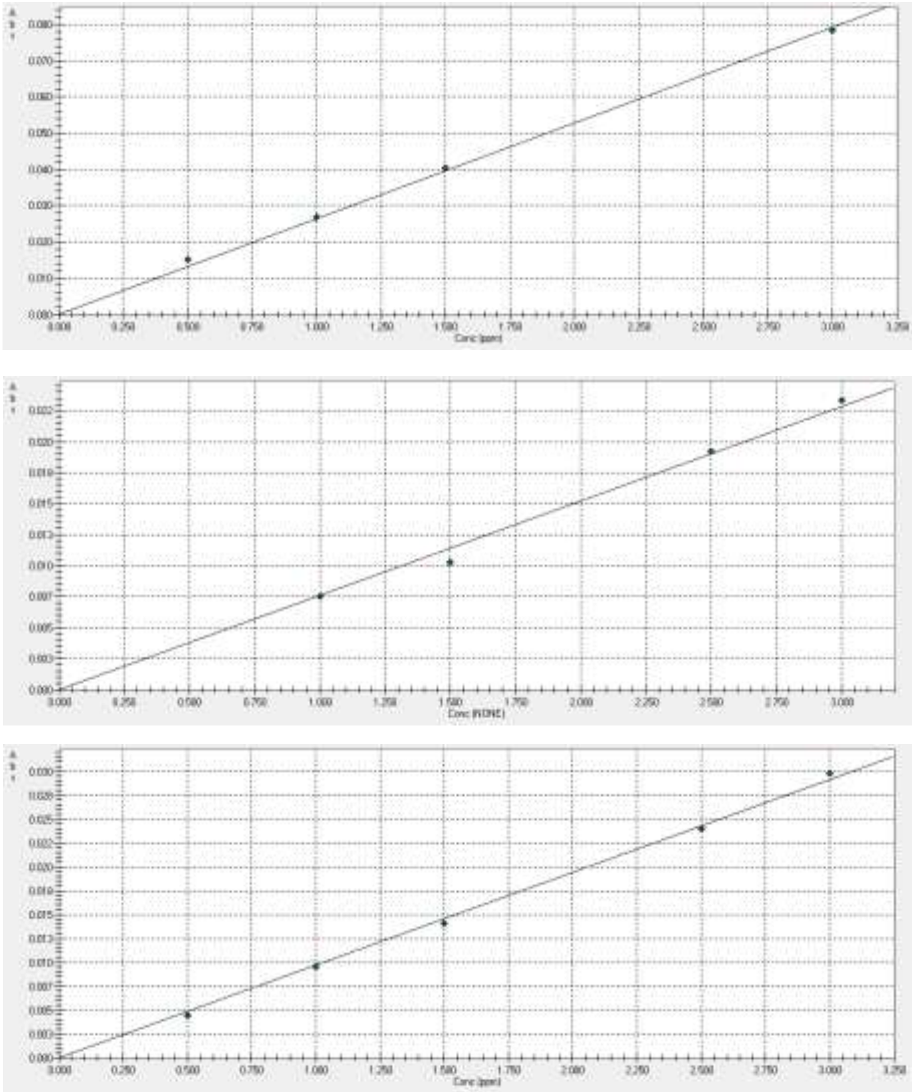
Figure 2- showed: A- discharged industrial water from tannery plants, B- groundwater in brick quarries

Materials and Methods

Samples of well water, untreated industrial wastewater and water used in different stages of tanning were obtained. Soil samples were obtained from various sites within the tanning plants area and from the quarry soil used in the brick industry. Using (Flame Atomic Absorption Spectrophotometry), (AA-6200), Shimadzu, Japan, for selected heavy elements (Pb, Ni, Cd and Cr) in water and soil samples. The method of operation of the device depends on the principle that the elements in their atomic state absorbs light with a certain wavelength of the Hallow Cathode Lamp of the element to be analyzed, as the device sets the concentration of the element in the solution after the evaporation of part of the solution by the heat of a gas torch Acetylene reaches more than (2000 ° C). GPS device, Garmin, USA, was used to determine the samples sites within the current study. Portable digital devices used in water samples to measure the values of pH, electrical conductivity, turbidity meter (UK) and total dissolved salts (TDS) (Romania). The samples were taken on depth of 10-20 cm from surface. Soil digestion procedure [13] was as follows:

1. Crushing the sample by porcelain mortar.
2. Putting the sample in clean and dried beaker and dried the sample on 100 ºC for two hours.
3. Weight 1 gm of dried sample and put it in dried clean beaker.
4. Adding 15 ml of concentric HCl with 5 ml of concentric HNO_3.
5. eating the sample on sand path till the ending of the brown fumes, then to dryness.
6. Cooling the beaker and then add 5 ml of HCl and heating till dryness.
7. Cooling the beaker and add 5 ml of HCl and 50 ml of hot distilled water to wash sides of beaker.
8. Heating the mixture to boiling for 2-3 minutes.
9. Filtering the solution by filter paper of 42 No.(whatman 0.42) and put the filtered solution in volumetric flask of 100 ml.
10. Washing the insoluble residue by distilled water and adding the washing water to the filtered solution and then complete the volume to 100 ml.

Figure -3 represents the calibration curve for heavy elements (Pb, Ni, Cd and Cr) using Flame Atomic Absorption Spectrophotometry device



Ni

Pb

Cd

Figure 3- The calibration curve for heavy elements (Pb, Ni, Cd and Cr)

Results and Discussion

Water samples

pH: The results in (Table -1) shown that pH value of well water samples as well as Nahrawan village water were within the permissible limits (6.5-8.5), while the highest pH value recorded in water sample (4) was (12.8), due to the addition of ($Ca(OH)_2$), so that the water becomes alkaline because deposition from the soil. The lowest value of pH recorded in sample (7) was (0.29), due to the addition of (H_2SO_4) in the acidification phase.

TDS: The highest value of TDS recorded in water sample (4) was (7800 ppm), (Table -1), due to increased water salinity by use of ($Ca(OH)_2$). While the lowest TDS value in water sample (6) was (539 ppm), due to the mixing of water out of the phase of removing the water with the previously unused water. Most of the registered TDS values for wastewater exceeded the water sample of the village of Nahrawan (860 ppm).

EC: The results, (Table -1) shows that the highest value of EC recorded in water sample (4) was (8200 μS / cm), while the lowest value recorded in sample (6) was (683 μS / cm). The value of EC for most water samples was high, including well water samples in the site, due to the use of different salts in the tanning operations, as well as the tanker water which brings from Nahrawan village and well water because ground water is shallow and salt in that area.

Table 1- Values of some chemical properties and concentration of heavy metals in the water samples of tanning plants in Nahrawan

	Site	pH	TDS	EC	Turbidity	Pb	Ni	Cd	Cr
1	Well water	7.6	929	5120	3.8	0.05	BDL	BDL	BDL
2	Tanker water	7.07	660	3800	1.81	BDL	BDL	BDL	BDL
3	After cleaning by water and salt	6.09	5390	7400	549	0.15	0.8	BDL	BDL
4	After add ($Ca(OH)_2$).	12.8	7800	8700	2.3	0.25	0.1	BDL	BDL
5	After remove ($Ca(OH)_2$).	5.9	1712	3160	1.95	0.3	0.2	BDL	BDL
6	Before cleaning by (H_2SO_4)	9.04	539	683	57.6	0.1	0.1	BDL	BDL
7	After cleaning by (H_2SO_4)	0.29	810	850	557	0.6	0.4	BDL	BDL
8	External discharge channel	6.88	6110	6200	116	3	5	BDL	BDL
9	Well water	7.3	853	4160	2.9	0.1	0.2	BDL	BDL
10	Well water	7.1	799	3520	2.12	0.04	BDL	BDL	BDL
11	Well water- Nahrawan village	7.2	860	1240	1.75	0.01	BDL	BDL	BDL
Iraqi standard for discharge water 1967		6.5-8.5	-	-	-	0.1	0.2	0.01	0.1

Turbidity: The results indicated that the highest value of turbidity for drained water recorded in sample (7) was (557 NTU), while the lowest value recorded in sample (5) was (1.95 NTU). Also, the lowest values of turbidity in the well water and the water sample of Nahrawan village.

Heavy Metals

The samples of discharged industrial water from tanning plants contained relatively high concentrations of heavy metals (Pb and Ni). These meals have the ability to accumulate and accumulate in sediments, which are discharged into external drainage channels, causing soil pollution in the area and then filtering into groundwater. Therefore, showed concentrations of Pb recorded in well water samples, while Ca and Cr concentrations were not detected in these samples, especially because Cr was not used in the tanning process.

Pb: The highest concentration of Pb in discharged water from tanning plants recorded in water sample (8), which represents the external discharge channel was (3 ppm), while the lowest concentration in sample (6) reached (0.1 ppm). Also, note that the concentration of Pb in most samples of discharged and untreated water exceeded the Iraqi standard (0.1 ppm), (Table -1), while the results showed low concentrations of Pb in the well water samples inside the tanning area including the Nahrawan water samples.

Ni: The highest concentration of Ni in discharged water from the tanning plant recorded in water sample (8), which represents the external discharge channel (5ppm), while the lowest concentration (6.4) was recorded (0.1 ppm). The concentration of Ni in most of the discharged and untreated water samples exceeded the Iraqi standard (0.2 ppm), (Table -1). Also, did not sense the concentration of Ni in the well water samples within the study area, while the concentration of Ni in the water sample of Nahrawan village was (0.007 ppm), which is much lower than the Iraqi standard (0.2 ppm).

Soil Samples

The results of the analysis of the soil samples, (Table -2) from different sites within the tanning area and the bricks quarry soil, showed relatively high concentrations of Pb and Ni, while Ca and Cr concentrations were not detected in these samples.

Pb: The highest Pb concentration recorded in soil sample (199 ppm) in the east of tanning plants, while the lowest concentration (51ppm) recorded in the middle of the brick quarries. The results in (Table -2) shown that the highest concentration of the Pb recorded in the soil samples that located in the east and south-east tanning plants and south of brick quarries, because the most active tanning plants are discharged their wastewater to the east and north of the region. Therefore, the nearby brick quarries are affected by the tanning plants that located on the southern boundary of the quarries. The tanning plants area are also affected by air pollutants released from the brick factories, as they fall within the course of the movement of these pollutants, making them susceptible to high concentrations of heavy metals, especially Pb. Results shown that Pb concentration in soil samples were within the limits of the Iraqi standard (50-300 ppm) for all sampling sites.

Table 2- concentration of heavy metals in soil samples

	Site	Pb	Ni	Cd	Cr
1	West of tanning plants	81.9	9.3	BDL	BDL
2	South-east of tanning plants	188.7	110	BDL	BDL
3	East of tanning plants	199	124	BDL	BDL
4	North of tanning plants	99.8	3.7	BDL	BDL
5	South of brick quarries	186	7	BDL	BDL
6	Middle of brick quarries	51	4.4	BDL	BDL
7	East of brick quarries	53	6	BDL	BDL
Iraqi standard (Ministry of Environment 2010)		50-300	30-75	1-3	---

Ni: The highest concentration of Ni in the soil samples was (124 ppm) in the east of the tanning plants, while the lowest concentration recorded in the northern region of the plants was (3.7 ppm). The results shown that the highest concentration of the Ni recorded in soil samples located east and southeast of tanning plants, exceeding the Iraqi standard for Ni concentration in soil (30-75 ppm), while the concentration of Ni in other soil samples within Iraqi standard, showed in (Table -2).

Conclusions and Recommendations

The results shown that the discharged wastewaters from the tanning plants contained high concentration of TDS, EC and turbidity, most of which were higher than the Iraqi standard. This is due to the significant use of salts in the production stages of tanning operations. The discharged wastewater samples from the tanning plants included relatively high concentration of Pb and Ni. These metals have the potential to accumulate in soil and groundwater, which are discharged to the external discharge channels, while the Ca and Cr concentration are not sensitized in these samples. The results of the analysis of the soil samples from different sites within the plants area and from the soil of brick quarries have shown relatively high concentration of Pb and Ni, within the limits of the Iraqi standard for the Pb, while the Ca and Cr concentration were not detected in these samples. The study showed the effect of air pollutants released from the nearby brick factories that located north of the tanning plants, as they fall within the course of the movement of these pollutants, making them susceptible to high concentration of heavy metals, especially Pb. Restart the Central Processing Unit, because it is important to dispose of heavy metals before putting waste into the environment. Sewage drains shall be isolated from each other and the recycling of these materials.

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