

original article

Dye removal from wastewater using shrimp chitosan as an eco-friendly adsorbent

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ABSTRACT

Aims: In this research, application of fishery wastes as locally available, cheap, eco-friendly, non-toxicity, reusable, abundant biodegradable resources and highly efficient adsorbent was studied for Direct Blue-86 (DB-86) removal from aqueous solution.

Materials and Methods: Comparison of the adsorption of DB-86 by chitosan produced from three different fishery wastes (shrimp, crab and squid collected from Persian Gulf) has been investigated. Effects of adsorbent dosage, pH, flow rate, ionic strength, interfering ions and dyes were evaluated.

Results: The results indicated that maximum removal of dye (~ 100%) was obtained by passing 100 mL of DB-86 (50 mg L⁻¹, pH=2) through a column containing 0.5 g chitosan by using continuous method (fixed-bed) at room temperature (25 ± 2 °C). Maximum desorption of 72% was achieved at alkaline medium (pH=13.5). It was shown that equilibrium isotherm could be fitted by the Langmuir equation. The maximum adsorption of chitosan (qm) and the energy of adsorption were calculated as nearly 60 mg/g and 3.6 mg⁻¹, respectively.

Conclusion: Chitosan was successfully used for removal of DB-86 from spiked Karoon River sample and the effluent of Pars Paper Factory, a local pulp and paper factory in Ahvaz. Results represent of three replicated experiments.

Key words: Chitosan, direct blue-86, dye removal, pulp and paper factory, wastewater treatment

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INTRODUCTION

A large number of industries such as textile, cosmetic, paper, and pulp consume large amounts of organic dyes. Effluents of these industries contain undesired quantities of organic dyes and need to be treated. It is reported that the annual production of nearly 100,000 commercial dyes is about 7×10^5 tonnes.^[1] Dyes are commonly toxic and hazardous to the environment. During past decades, many methods

for dye removal from wastewaters have been reported. These methods include chemical coagulation, oxidation, ozonation, irradiation, precipitation, and adsorption.^[2-4]

Adsorption is an effective and economic method for the removal of dyes. Activated carbon is a widely used adsorbent

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for removal of most of dyes because of high capacity for adsorption of different dyes, but its use is limited because of high cost. A large variety of low-cost adsorbents as an alternative of activated carbon have been investigated for their ability to remove dyes.^[5,6]

Chitosan is a polysaccharide having a long chain that its commercial form has an average molecular weight between 3800 and 20,000 Daltons. Chitosan is synthesized from deacetylation of chitin, a naturally occurring polysaccharide (in shell-fish sources such as shrimp, crab, and squid). Synthesized chitosan is identified by its degree of deacetylation (DD), the ratio of the number of amine groups to the sum of the number of amino and acetyl groups in chitosan. DD in commercial chitosan is often between 66% and 95%. Due to the presence of amino groups (hydrophobic group), chitosan is insoluble at basic pH. Because of protonation of amino groups, it is soluble in acidic pH. Chitosan is biocompatible, biodegradable, anti-microbial, and nontoxic agent. It is easily converted into various forms such as gels,^[7] membranes,^[8] nanofibers,^[9] beads,^[10] micro- and nano-particles,^[11] and sponges.^[12] Chitosan as a biosorbent for the removal of dyes and heavy metal ions has been studied.^[13-16] Advantages of chitosan are low cost compared to activated carbon and excellent chelation behavior toward heavy metal ions. Chitosan has many applications in agriculture, waste water treatment, cosmetics, drug-delivery, balance diet, artificial skin, and medical applications.^[17-23] Chitin and chitosan have been found in wide range of natural sources such as crustaceans, annelida, mollusca, spiders, ants, and fungi.^[24] The production of chitosan is economically based on crustaceans (crab and shrimp shells) and it is feasible because of inexpensive chemical reagents and mild production conditions. Producing 1 kg of chitosan (70% DD) requires 6.3 kg HCl and 1.8 kg NaOH.^[19,24] The most crucial limitation that is encountered in the implementation and use of chitosan is collection and supply of the appropriate quality raw materials due to quick corruption of fishery wastes. Purpose of this study is to explore the applicability of chitosan as an eco-friendly adsorbent for the removal of direct blue-86 (DB-86) from industrial effluents using continuous method (fixed-bed). Effects of various parameters (adsorbent dosage, pH, flow rate, ionic strength, interferent ions, and dyes) on the performance of adsorption process were investigated.

MATERIALS AND METHODS

Materials

The industrial DB-86 was obtained from a local paper manufacturer and currently among the widely used commercial dyes in the printing of cotton, dyeing of silk wool and vinylon.^[25] All other chemicals used were analytical grade and purchased from MERCK Co., Germany. The chemical structure of DB-86 ($C_{32}H_{14}O_6N_8S_2CuNa_2$) was shown in Figure 1.

The concentration of aqueous solutions of DB-86 was determined from the calibration curve that was obtained by measuring the absorbance of standard solutions of DB-86 at $\lambda_{max} = 619$ nm by ultraviolet-visible spectrophotometer (Perkin Elmer, model 550S, USA). Different concentrations of DB-86 were prepared from stock solution (100 mg/L) by dissolving appropriate amount of DB-86 in distilled water.

Preparation of chitosan

The shells of shrimp (crab or squid) were washed three times with distilled water to remove impurities, and air dried and crushed to a powder form. Then, it was deproteinized by NaOH (5% w/w) and immersed in HCl (10% w/w) for removal of all minerals, especially $CaCO_3$, for 18 h. The product (chitin) was rinsed several times with deionized water and then deacetylated in NaOH (50% w/w) at 90°C for 3 h. The resulting powder (chitosan) was filtered and rinsed three times with deionized water and dried at 50°C for 12 h and sieved in the size range 30–80 mesh (0.595–0.177 mm).^[16] The chemical structures of chitin and chitosan are shown in Figure 2.

Characterization of prepared chitosan

In this study, several physical properties of prepared chitosan were measured. According to Guibal *et al.* method,^[26] DD was determined by infrared (IR) spectroscopy (72.0%). DD is determined by applying the following equation:

$$DD = 97.67 - (26.486 [A_{1655}/A_{3450}])$$

where A_{1655} and A_{3450} are the absorbance values of the amide groups at 1655 cm^{-1} and the absorbance value of the hydroxyl groups at 3450 cm^{-1} , respectively. The IR spectrum of chitosan is shown in Figure 3. The analysis of hydrogen, carbon, and nitrogen was performed by CHNS Analyzer (Thermo Finnigan, Flash EA 1120 Series, USA). The results are %H, 3.4868; %C, 24.4285; %N, 3.2668.

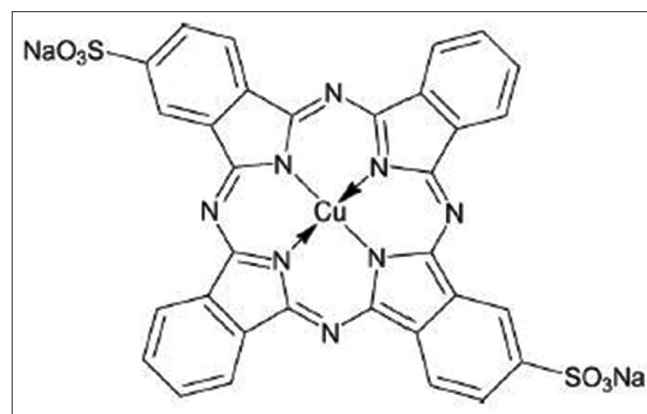


Figure 1: The structure of direct blue-86, molecular weight = 778.96 g

Adsorption procedure

A glass tube (7 mm × 70 mm) with a very fine bore was used as a column. It was filled with 0.5 g of chitosan (40 mm of column, dried at 50°C for 24 h). The column was washed first with water at room temperature. Aqueous solutions (100 mL, pH = 2) containing different amounts of DB-86 were passed through the column at room temperature. The absorbances of aqueous solutions before and after passing the column were measured at $\lambda_{\max} = 619$ nm by spectrophotometric method. The percent removal of DB-86 (%R) was calculated using the following formula (%R), where C_i and C_f are initial and final concentrations of aqueous solutions of DB-86, respectively.

$$\%R = \left(\frac{C_i - C_f}{C_i} \right) \times 100.$$

RESULTS

The effect of adsorbent dosage was studied at different amounts of chitosan in the columns and the obtained results are illustrated in Figure 4. Effect of solution pH, flow rate of column and electrolyte concentration (ionic strength) on adsorption capability of chitosan was studied and obtained results are shown in Figures 5, 6 and 7, respectively. In addition, Desorption of DR-86 dyes from chitosan surface and presence of other ions and dyes was investigated and presented in Figure 8 and Table 2.

DISCUSSION

Comparison of the adsorption of three different fishery wastes

Three columns containing 0.2 g of three types of chitosan of shrimp, crab, and squid were prepared and 100 mL 30 mg/L of DB-86 was passed through each column. Primarily results showed chitosan prepared from shrimp was more efficient for DB-86 adsorption compared to the others. Table 1 lists the obtained results.

Effect of experimental parameters of dye removal

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by passing 100 mL of aqueous solution of DB-86 (pH = 2) through the columns containing different amounts of chitosan (0.1, 0.2, 0.3, 0.4, and 0.5 g) at room temperature. Results are shown in Figure 4. The percent removal of DB-86 was increased significantly

Table 1: Effect of source of chitosan on the removal of direct blue-86

Type of chitosan	Removal of DB-86 (%)
Shrimp chitosan	46.16
Crab chitosan	43.13
Squid chitosan	32.76

DB-86: Direct blue-86

with increasing adsorbent dosage. The increased adsorption with adsorbent dosage can be attributed to increased adsorbent surface area of adsorbent and the availability of more adsorbent sites.

Effect of pH

The pH value of the solution is an important parameter in the adsorption process. The effect of pH was investigated by passing 100 mL of aqueous solutions of DB-86 (50 mg/L) with different pH values through the columns containing 0.5 g of chitosan at room temperature. The results are presented in Figure 5. The maximum dye removal is obtained at pH = 2 (95%). The dye removal was decreased by increasing pH from 2 to 9. Therefore, the pH of solution was adjusted at pH = 2 by glycine-HCl buffer in further studies.

Effect of flow rate

Flow rate is another variable in adsorption process. In

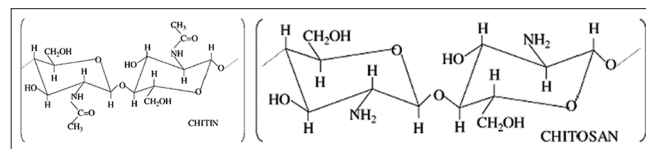


Figure 2: Structures of chitin and chitosan

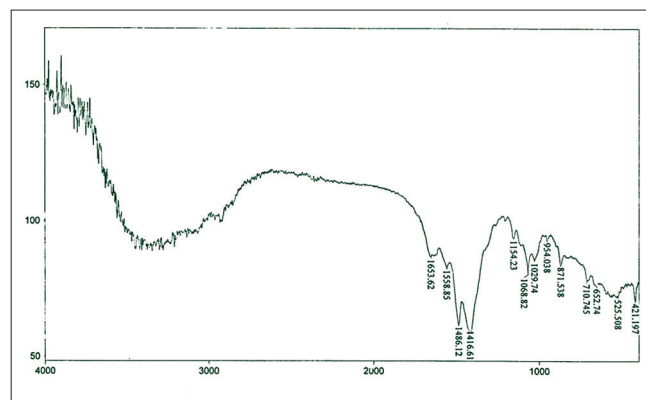


Figure 3: Infrared spectrum of chitosan

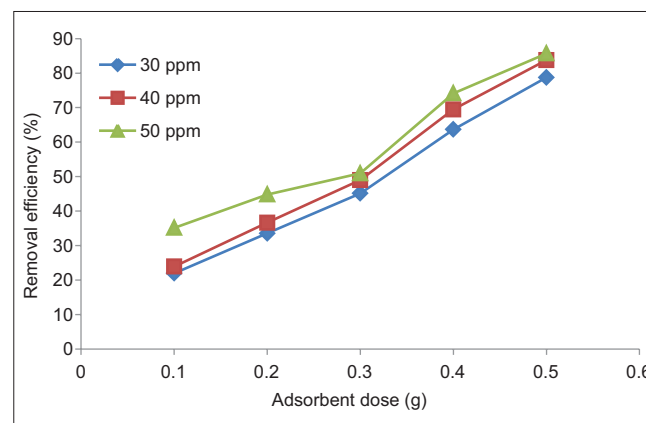


Figure 4: Effect of adsorbent dosage

general, the removal efficiency of dyes is increased by decreasing flow rate (leading to prolonging contact time). To study the effect of flow rate on removal efficiency, 100 mL of aqueous solution (pH = 2) of DB-86 (50 mg/L) was passed through the column containing 0.5 g of chitosan at different flow rates at room temperature. The results are shown in Figure 6.

Effect of electrolyte concentration

An important factor is the effect of electrolyte concentration (ionic strength) on dye removal efficiency. Furthermore, some of the electrolytes such as NaCl are often used as a stimulator in dyeing process. The presence of electrolyte can increase or decrease dye removal efficiency either by screening between charged adsorbent and adsorbing molecule or by adsorbing on charged sites of the adsorbent.^[27] To investigate the effect of ionic strength, aqueous solutions of DB-86 (50 mg/L) containing different amounts of NaCl (0.1–0.6 M) were passed through the column containing 0.5 g of chitosan at room temperature. The results [Figure 7] showed that removal efficiency

was increased (~100%) by increasing sodium chloride concentration.

Desorption experiment

Desorption of dyes is interesting for textile industries because dyes from effluents can be adsorbed, concentrated, and reused for keeping the process costs down. After passing the aqueous solution of 50 mg/L of DB-86 through column containing 0.5 g chitosan and dye removal by the column, desorption process was carried out by passing 100 ml NaOH solution as eluent with different pH (8–13.5) through the column. In accordance with the results, the desorption (%) was about 72% at pH = 13.5. Therefore, desorption (%) was

Table 2: Effect of foreign ions on the removal of direct blue-86

Ion/direct blue-86	Interferent ions
1000	Na ⁺ , K ⁺ , NH ₄ ⁺ , Co ²⁺ , Al ³⁺ , Br ⁻ , Cl ⁻ , F ⁻ , I ⁻ , EDTA*, NO ₃ ⁻ , NO ₂ ⁻
500	Ag ⁺ , Ca ²⁺
100	Ni ²⁺ , Cu ²⁺ , Cd ²⁺
1	Fe ³⁺ , SO ₄ ²⁻ , PO ₄ ³⁻
1	Neutral red, orange (II), direct yellow, methyl orange

*EDTA: Ethylenediaminetetraacetic acid

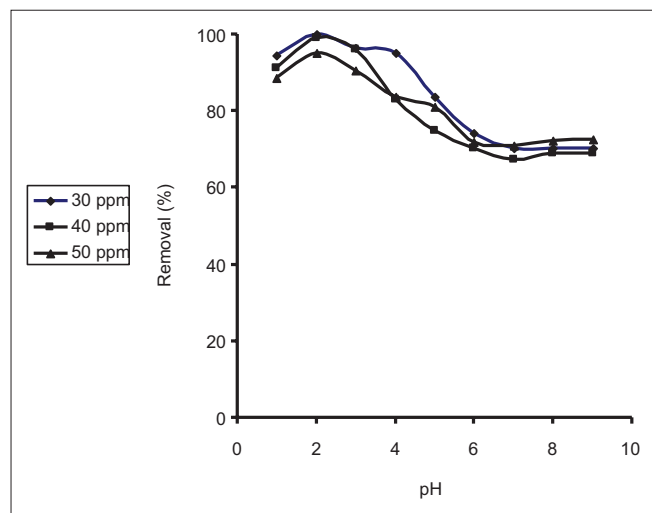


Figure 5: Effect of pH

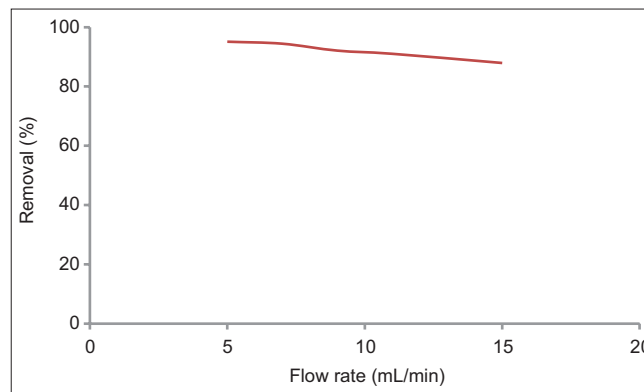


Figure 6: Effect of flow rate

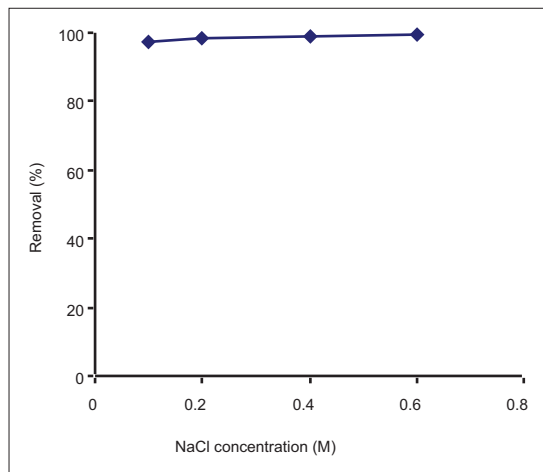


Figure 7: Effect of electrolyte concentration

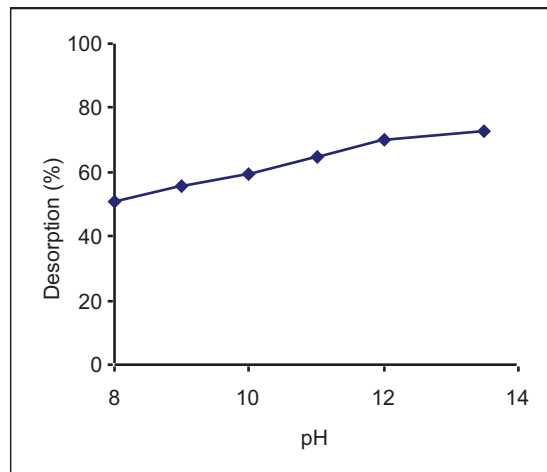


Figure 8: Effect of pH on desorption of direct blue-86

increased with an increase in pH of the eluent. The results are shown in Figure 8.

Effect of interfering ions and other dyes

The presence of other ions and dyes might affect the adsorption process. The effect of foreign species was examined by passing aqueous solutions (pH = 2) of DB-86 (50 mg/L) containing foreign species through the column containing 0.5 g of chitosan at room temperature. The results are shown in Table 2. In the presence of some of metal ions such as Fe³⁺, color removal was decreased due to complex forming between Fe³⁺ and chitosan.^[28] On the other hand, the presence of high levels of Ni²⁺, Cd²⁺, Co²⁺, Al³⁺, K⁺, Br⁻ did not significantly decrease the adsorption of DB-86. Finally, in the presence of other dyes and their competitive adsorption on chitosan sites, removal efficiency was decreased.

Batch adsorption experiments

Batch adsorption studies were performed by stirring 100 mL of aqueous solutions (pH = 2) containing different concentrations of DB-86 (40–90 mg/L) and 0.1 g of chitosan at room temperature. The different suspensions were stirred until equilibrium condition was reached (24 h). Based on batch experiments, the amount of dye adsorbed on chitosan at equilibrium (q_e) at different concentrations of DB-86 was obtained as follows:

$$q_e = \frac{V(C_o - C_e)}{m}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentration of DB-86, V is solution volume (L), and m (g) is the dosage of chitosan. Based on the results in Figure 9, maximum adsorption capacity of chitosan (q_m) was determined as nearly 60 mg/g. The linear plot of C_e/q_e against C_e [Figure 10] indicates the adsorption of DB-86 obeys Langmuir isotherm model. According to Langmuir equation:

$$C_e/q_e = 1/Kq_m + C_e/q_m$$

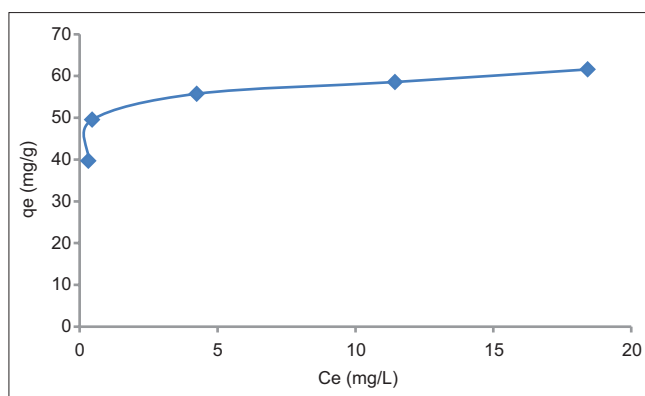


Figure 9: Variation of q_e against C_e

q_m and K (energy of adsorption) were determined from the slope and intercept of the plot. Their values are 61.7 mg/g and 3.6 mg⁻¹, respectively.

Application

To investigate the reliability of the proposed method, it was applied to the removal of DB-86 from industrial water samples. For this purpose, 100 mL of the sample was treated under the general procedure. The results presented in Table 3 show that good extraction efficiency is obtained and confirm the validity of the proposed method for real samples.

CONCLUSION

Chitosan effectively can be used to remove DB-86 from industries effluent. Chitosan is locally available, cheap, and reusable. This natural polymer is an effective adsorbent for removal of large amounts of DB-86 up to 300 mg/L in optimal operating conditions. The most important parameter on the adsorption process of DB-86 by chitosan is pH. In acidic solution, the strong electrostatic interaction is formed between protonated amino acids in chitosan and anionic dye. Thus, the maximum removal of DB-86 was obtained at pH = 2. In other words, at more acidic solution, more R-NH₃⁺ on the surface of chitosan is formed, and more attraction exists between the positively charged surface of chitosan and anionic dye DB-86. Similar results are reported by Mahmoodi *et al.* and Chiou *et al.*^[29,30] In an alkaline

Table 3: Applicability of removal method in real and spiked aqueous samples

Sample	Concentration of DB-86 (ppm)		Removal (%)
	Before removal procedure	After removal procedure	
Karoon river	ND*	ND*	-
Spiked Karoon river	50.0	2.40	95.0
Effluent of pars paper factory	28.5	0.24	99.5

*ND: Not detected, DB-86: Direct blue-86

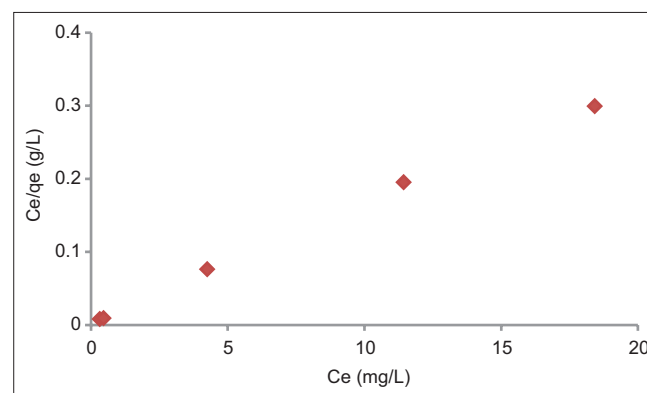


Figure 10: A plot of C_e/q_e against C_e for the adsorption of direct blue-86 on chitosan powder

medium, positively charged chitosan was deprotonated in an alkaline medium so that the attraction between chitosan and anionic dye becomes much weaker. As a result, anionic dye departed from active site of chitosan.^[27,31] In alkaline medium (pH = 13.5), DB-86 is desorbed (72%) from chitosan. Therefore, chitosan is reused and regenerated for many times.

Finally, chitosan was successfully used for the removal of DB-86 from spiked Karoon River sample and the effluent of Pars Paper Factory sample, a local pulp, and paper factory in Ahvaz. The equilibrium data using batch system correlated well with the Langmuir adsorption model. Maximum capacity of chitosan was calculated (nearly 60 mg/g). Based on this study, one could conclude that chitosan as an eco-friendly adsorbent can be used for dye removal from wastewater of different industries such as paper and pulp.

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Conflicts of interest

There are no conflicts of interest.

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