Utilization Of Egg-Shell, A Locally Available Bio-waste Material, for Adsorptive Removal of Congo Red From Aqueous Solution

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Abstract – Egg-shell, a locally obtainable biowaste material, was successfully used for common textile dye (congo red) removal from synthetic wastewater solution. All adsorptive experiments were carried out in a batch method. Experiments were conducted to understand the consequence of different functioning parameters, for example, the pH of the solution, adsorbent dosage, reaction time, and initial adsorbate concentration. The surface morphology of the egg-shell was analyzed by scanning electron microscopy (SEM) images of the adsorbent (before as well as after adsorption) showed that there was a change in surface morphology, which ensured the congo red adsorption on the adsorbent surface. The adsorbent dose was determined to be 1g as optimum value, while the solution pH 5 was seemingly the best operating pH at the tested conditions. Complete adsorption was achieved in 120 min while the pseudo-second-order kinetic model portrayed the sorption kinetics quite nicely. Langmuir adsorption model (monolayer adsorption) was the best-suited model for describing the sorption process in the concern of the correlation coefficient. The values of dimensionless separation parameters ($R_L$) signified that the adsorption process was promising for all studied concentrations. A considerably great extent of sorption capacity (153.85 mg/g) of egg-shell adsorbent indicated that it could be employed for wastewater treatment in textile and related industries.

Keywords: Adsorption; Egg-shell; Congo red; Isotherm; Kinetics.

Introduction

Wastewater treatment is a challenging task in the majority of the industry due to environmental concerns. The textile industry is the primary dye consuming sector where more than 10,000 tons of total dye consumed every year in this sector throughout the world (Yagub et al., 2012). Annually about 100 tons of dye is discharged into a river, damaging the marine and human life (Yagub et al., 2012). In Bangladesh, the effluents from the textile industries are usually discharged into the river that causes severe water pollution (Mozumder and Islam, 2010). Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, abbreviated as CR), enormously used in dyeing textiles, is an azo dye having an aromatic ring structure. The mutagenicity of azo dyes can cause some types of cancer, and because of this, it is banned in many countries (Asses et al., 2018; Myslak et al., 1991). Due to the synthetic as well as the complex aromatic structure of dye, it is more challenging to eliminate such dye from wastewater (Srinivasan and Viraraghavan, 2010). There are numerous chemical, biological, and physical removal methods. These include but not limited to coagulation (Shi et al., 2007), oxidation (Errugay and Acar, 2017), chemical treatment (Wang et al., 2007; Mishra and Bajpai, 2006), electrochemical methods (Gupta et al., 2007), ion-exchange (Raghu and Basha, 2007) and adsorption. Among them, adsorption is recognized as the most common and cost-effective technique for the treatment of wastewater. Several adsorbents (both natural and artificial) have been used in dye removal purposes. Although activated carbon other commercial adsorbents are thought to be very effective adsorbents, those are costly and difficult to dispose of (Mall et al., 2005). Taking these facts into consideration, researchers...
around the globe search for alternative sources of adsorbents. Many waste materials and biomaterials are reported to be utilized for adsorption purposes. These materials include but not limited to orange peel (Munagapati and Kim, 2016), coconut tree bark (Parvin et al., 2019b), egg-shell (Abdel-Khalek et al., 2017), egg-shell membrane (Arami et al., 2006; Parvin et al., 2019a), Aspergillus niger (Asses et al., 2018), sawdust (Taty-Costodes et al., 2003), and banana peels (Annadurai et al., 2002).

The egg-shell is mainly the outer shield of the hard-shelled egg, and the weight of this shell is 11% of the overall weight of a single egg. The constituent materials of egg-shells are CaCO₃, MgCO₃, Ca₃(PO₄)₂ and various organic matters, while the percent distributions are 94%, 1%, 1%, and 4%, respectively (Lokaewmanee et al., 2014). However, the number of egg production in Bangladesh was 1710.79 billion in the fiscal year 2018-19 (Website of Dhaka Tribune, 2019). After consumption, these egg-shells are generally discarded in the land without its further use. Carvalho et al. (2011) estimated that a single egg-shell contains some pores (e.g., between 7,000 and 17,000) that makes it more attractive adsorbent material for dye removal. A large number of research initiatives have been conducted on the application of egg-shell, and it can be shown that egg-shell can adsorb heavy metals as well as organic matter (Koumanova et al., 2002). Several studies have been documented where egg-shell was applied as an adsorbent for dye removal purpose all over the world (Pramanpol and Nitayapat, 2006; Tsai et al., 2006). However, almost no research has been done on the proper utilization of egg-shell, an available waste material from the poultry sector, in the context of Bangladesh. Therefore, the preparation of adsorbent using a low-cost, efficient, and easy-to-use material (egg-shell in this case) and its successful utilization for dye removal would be a great task in the view to environmental remediation in Bangladesh.

In this present batch study, congo red (CR) contained synthetic wastewater was used by authors for the experiment. Egg-shell is locally available, and for this experimental study, egg-shells were collected from the student’s residential hall of Jashore University of Science and Technology, Jashore, Bangladesh, as well as restaurants nearby the university. Through a systematic process description, this study also explains the effects of the number of operative parameters such as the solution pH, adsorbent dosage, contact time between adsorbent and adsorbate, and initial concentration were investigated for the congo red (CR) removal through adsorption. Appropriate techniques examined the adsorbent surface morphology, the equilibrium data were analyzed by extensively used isotherm model in the adsorption research field, and kinetic data was examined by two different kinetic models to perceive the performance of the adsorbent and, at the same time to understand the inherent adsorption mechanism.

Materials and Methods
Preparation of adsorbent and its characterization
Egg-shells are available as waste material. The waste egg-shells (irrespective of the color of the egg-white or brown, and also irrespective of hens and ducks) were amassed from the central cafeteria of the students’ residential halls of Jashore University of Science and Technology, Jashore 7408, Bangladesh, and from the restaurants situated nearby the university campus. To remove dirt from the surface, egg-shells were successively washed with tap water and distilled water. After that, the egg-shells were dried at about 105°C in an oven (Model-SLN 53 STD, Pol-Eku-Aparatura, Poland) for about one h. Then the dried egg-shells were ground initially using mortar and pestle and finally using a blender to make it powdery form. The powdered egg-shell was soaked with 0.1M H₂SO₄ at a ratio of 1:1 (weight: volume) for overnight to activate the sorption sites as well as to improve adsorption efficiency and then treated with 2% NaHCO₃ solution so that excess acid is removed (Belay and Hayelom, 2014). After that, the egg-shell suspension was neutralized by thoroughly washing with distilled water and then filtered and dried. The moisture content, as well as bulk density, was measured. The moisture content was determined by the weight loss-on-drying (LOD) method, where a balance and an oven were utilized while the bulk density was determined by measuring the mass of a known volume of the dried sample. Lastly, the sample was stored in an air-tight bottle from where the adsorbent sample was used. The preparatory steps are shown in Fig. 1. To understand the morphology of the adsorbent, the microscopic analysis was performed with a scanning electron microscope (Model-S3400N, Hitachi, Japan). In addition to that, to know about the surface functional groups present in the adsorbent, a Fourier Transform Infrared (FTIR) spectroscopic analysis was conceded out too with FTIR spectrometer (Model-8400S, Shimadzu, Japan).
Figure 1. Steps to prepare dried powdered adsorbent derived from egg-shell.

**Chemicals**

According to the IUPAC method, the name of congo red is disodium 4-amino-3-[[4-[4-[[1-amino-4-sulfonatonaphthalen-2-yl]diazenyl]phenyl]phenyl]diazenyl]naphthalene-1-sulfonate with a molecular formula of C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}. The CR is a chemical compound containing an aromatic heterocyclic structure. The molecular weight of congo red is 696.7. The as-received analytical grade CR was used in this experimental work. The used chemicals such as sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium bicarbonate (NaHCO₃), sulfuric acid (H₂SO₄), and other chemicals were of reagent grade. A stock solution (1000 ppm or mg/L) of CR was prepared, which was further diluted to make working solutions of congo red of requisite concentration.

**Adsorption studies**

The adsorption investigations were accomplished to determine optimum conditions of the sorption parameters of the entire process, which includes the pH of the working solution, adsorbent dose, contact time, and initial concentration of working solutions. The impact of pH, adsorbent doses, contact times, and initial congo red dye concentration were studied in a 250 ml conical flask where 100 ml of adsorbate (CR dye solution) of identified concentration was added to a measured amount of adsorbent. The whole suspension was stirred for a specific time and at a particular temperature. The removal efficiency (%Re) of congo red and the sorption capacity (qₑ) of the adsorbent for CR removal were determined using the following two equations (Eq. 1 and Eq. 2):

\[ \% \text{Re} = \frac{C_i - C_f}{C_i} \times 100 \]  

\[ q_e = \frac{C_i - C_f}{w} \times V \]  

where \( C_i \) (mg/L) is termed as the initial dye concentration, \( C_f \) (mg/L) is denoted as the final dye concentration. At the same time, \( w \) (g) and \( V \) (L) are designated as the weight of the egg-shell powder and the solution volume, respectively. All experiments were accomplished two times, and the average value of those two values was considered for calculation. However, Microsoft Office Package (MS Excel) was used for data analysis in this study (Elabbas et al., 2016).

**Isotherm studies**

The adsorption characteristics of egg-shell powder were determined using two general models, namely, Langmuir isotherm model and Freundlich isotherm model. The mathematical expression of the linearized pattern of the Langmuir isotherm model, as well as the Freundlich isotherm model, can be stated by Eq. 3 and Eq. 4, respective (Parvin et al., 2019a).

\[ \frac{1}{q_e} = \left( \frac{1}{k_L \cdot q_m} \right) \left( \frac{1}{C_e} \right) + \frac{1}{q_m} \]  

\[ \log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \]  

where \( C_e \) is denoted as the equilibrium dye concentration (mg/L), \( q_e \) (mg/g) and \( q_m \) (mg/g) are termed as the adsorption capacity at equilibrium and the maximum capacity of adsorption, respectively, \( k_L \) is denoted as the
Langmuir isotherm constant (L/mg) related to the adsorption free energy, while $K_F$ (mg/g) and $1/n$ are designated as the capacity of adsorption at unit concentration and the intensity of adsorption, correspondingly.

**Kinetic studies**

In the present experimental study, the kinetics of adsorption techniques were investigated using two different models, namely, the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. For this, 1000 mg of adsorbent was added with a certain amount of congo red (100 ml) of known concentration. The temperature was kept constant. After shaking for a certain period, the solution was filtered, and the congo red dye concentration in the filtrate was measured. For analyzing experimental data, linear forms of the pseudo-first-order kinetic model and pseudo-second-order kinetic model were used, which can be stated as follows (Arami et al., 2006; Ho and McKay, 1998; Lagergren, 1898):

$$\frac{t}{q_t} = \frac{1}{k_1 q_{e,cal}} + \frac{t}{q_{e,cal}}$$

$$\log(q_{e,cal} - q_t) = \log q_{e,cal} - \frac{k_1 t}{2.303}$$

where $q_{e,cal}$ (mg/g) and $q_t$ (mg/g) are denoted as the adsorbed amount of congo red onto the adsorbent at equilibrium conditions and at contact time $t$ (min), respectively. $k_1$ (1/min) is termed as the adsorption rate constant for pseudo-first-order, and $k_2$ (g/(mg·min)) is termed as the adsorption rate constants for pseudo-second-order.

**Results**

**Adsorbent characterization**

**Moisture content**

The adsorbent’s moisture content was measured from the difference of weight of adsorbent before and after drying at a specific temperature for a specified period (Benzaoui et al., 2018). Approximately 5 g of adsorbent was taken in a convection type oven for 24 h at around 105°C. The sample was removed after that period and weighed again. The percentage of moisture content was calculated by weighing the primary and ending mass of the egg-shell adsorbent. The moisture content was found to be 4.17%.

**Bulk density**

Bulk density includes the mass of the adsorbent as well as the total pores of the material. It was determined with a simple procedure by using a measuring cylinder. A certain amount of adsorbent ($g$) was measured and kept in the measuring cylinder, and the volume occupied (cm$^3$) was determined. However, the bulk density of the powdered egg-shell was measured as 1.13 g/cm$^3$.

**Fourier transform infrared spectrum (FTIR)**

Fourier transform infrared (FTIR) spectrum in a wide range of 400 – 4000 cm$^{-1}$ was analyzed in the existing research to know the characteristics of the surface of the powdered egg-shell. Figure 2 shows the spectra of the adsorbent prior to adsorption (solid line) and after adsorption (dotted line) of congo red (CR) dye from synthetic solution. For egg-shell powder (before congo red adsorption), notable bands were found in 867.96, 1118.71, 1413.82, 1614.41, and 3300 – 3500 cm$^{-1}$, which could express the adsorbent characteristics. A band at the broad region of 3300 – 3525 cm$^{-1}$ can be assigned to the O–H as well as N–H stretching vibrations. This is the indication of moisture adsorption capacity of the egg-shell powder- since the OH group is present in it (Abdel-Khalek et al., 2017). The band at 1614.41 cm$^{-1}$ reveals a carbonyl group stretching (C=C stretching) of amide group as well as N–H bending (Aramai et al., 2006) while the band at 1413.82 cm$^{-1}$ reflects C – H stretching. Peaks at 1118.71 cm$^{-1}$ and 867.96 cm$^{-1}$ are associated with C – O stretching as well as C – H bending, correspondingly (Pavia et al., 1987; Website of Merck, 2020). The band at 1118.71 cm$^{-1}$ indicates the presence of secondary alcohol on the adsorbent (Website of Merck, 2020). It has been reported that the structure of congo red contains partially positive sodium ion (Bartošová et al., 2017). When the adsorbent comes into contact with congo red solution, hydroxyl ions are attached with a sodium ion, and the alkene compound is formed. However,
a new peak at 702.09 cm⁻¹ (C=C bending for alkene compound) has been observed after congo red adsorption (red dotted line in Fig. 2) by egg-shell powder.

Microstructural analysis with SEM

Scanning electron microscopic analysis was employed for observing the adsorbent surface morphology. Fig. 3(a) and 3(b) show the SEM images of egg-shell powder adsorbent for before and after congo red adsorption. It is evident that the egg-shell adsorbent is porous and has an agglomerated rough surface, as well as an irregular particle shape. This signifies that physical adsorption of congo red may occur on its surface (Abdel-Khalek et al., 2017). However, a noticeable change in the textural structure is found after congo red dye adsorption onto the surface of the egg-shell adsorbent.

Discussion

Effect of pH

In this adsorptive experiment, the pH of the wastewater solution is supposed to be a very significant parameter, which can affect the congo red dye adsorption onto the surface of the egg-shell powder adsorbent. Fig. 4 shows the removal percentage of congo red at a pH ranging from pH 3 to 9. From Fig. 4 it is evident that
the removal percentage of congo red rises from pH 3 to pH five at which it reaches the maximum value of adsorption (98.5%). After then the percent removal starts to decrease (though very slightly) throughout the studied range. Adsorption was favorable in acidic media. This may happen because of an electrostatic attraction between functional groups present in egg-shell adsorbent and sulfonate (SO$_3^-$) group of congo red (Al-Ghouti and Khan, 2018; Parvin et al., 2019a). With an increase in pH, electrostatic repulsion may occur between the negatively charged egg-shell powdered adsorbent surface and negatively charged sulfonate groups of the adsorbate. At the same time, competition among negatively charged hydroxyl ions (-OH) and congo red dye happens. Thus the congo red dye removal decreases slightly with the increase in pH. However, pH 5 was selected as the optimum pH for carrying out further experiments.

![Figure 4. Effect of pH on removal of CR dye onto powdered egg-shell at different pH.](image)

**Effect of Adsorbent Dosage**

Selecting the dosage of adsorbent is another vital task to do for the reason that this process defines the perfect adsorbent amount for performing removal experiments. Figure 5 shows the influence of adsorbent dosage. It is apparent from this figure that at a given condition, the percent removal of dye increases (from 96.5% to 99.5%) with an increase in adsorbent dosage (e.g., from 0.25 g to 1.0 g). Figure 5 also shows that after a specific dose of adsorbent, the removal percentage of adsorbate does not increase significantly. This might happen to owe to the fact that with the increase in the amount of adsorbent, the surface area, as well as the number of total dynamic sites, increases (Wu et al., 2014). However, based on this result, 1 g of egg-shell powdered adsorbent was chosen as an optimum dose for future experiments.
Effect of Contact Time

For determination of the exact reaction time, adsorption experiments are needed to carry out at varying contact time (between adsorbate and adsorbent). The effect of contact time on the adsorption efficiency of congo red is presented in Fig. 6. Such experimental findings represent the adsorbate (congo red) transfer kinetics to the egg-shell adsorbent surface. From Fig. 6, it can be comprehended that the removal percentage of dye increases progressively with the increase in time from 10 min to 90 min. About 95% of removal was found to be achieved in 90 min. After that, the percent removal did not increase significantly. However, for carrying out further adsorption tests, 120 min was taken to ensure a complete reaction. Two distinct phases of adsorption were evident from the figure. In the first phase, the rapid increase in adsorption rate is because of the accessibility of a huge number of active positions at the adsorbent surface. In the second phase, the adsorption becomes slower and lesser because the equilibrium phase is achieved. Similar findings were reported by various research groups (Pérez Marín et al., 2009; Elabbas et al., 2016).

Adsorption kinetics study

As stated in the earlier section, the kinetic studies for the congo red dye adsorption onto egg-shell powder surface were analyzed through two different kinetic models, namely, pseudo-first-order and pseudo-second-
order kinetic model. The well-fitted model was designated on the basis of the value of the coefficient of determination ($R^2$) as well as the extent of $q_e$ obtained from these models.

Using the pseudo-first-order kinetic model (stated earlier in Eq. 5), the extent of adsorbed amount ($q_{e,cal}$) of congo red and other necessary parameters were calculated. The calculated parameters were obtained from the intercept, and the slope of a straight line of plot $\log (q_{e,cal} - q)$ vs $t$ (figure not shown here) and the values are tabulated in Table 1. In a similar way, according to Eq. 6 (stated in the earlier section), the pseudo-second-order kinetic model was represented in Fig. 7. From the plot of $t/q_t$ vs $t$, a well-defined straight line is obtained. From the slope and the intercept of this plot, the values of the amount adsorbed ($q_{e,cal}$) and rate constant ($k_2$) were estimated and arranged in Table 1. As it is found from the table, the amount of adsorbate calculated (congo red) nicely matched with that of the experimental value. Moreover, the value of the coefficient of correlation or regression coefficient ($R^2$) of the pseudo-second-order kinetic model was very nearer to 1. In contrast, the $R^2$ value of the kinetic model for pseudo-first-order was merely 0.7117. Thus it is obvious that the rate of adsorptive interaction might be best-explained by the kinetic model of pseudo-second-order for the adsorption of congo red dye onto egg-shell powder. A similar result has been documented by several research groups for adsorption purposes (Wu et al., 2014).

![Figure 7. Adsorption of CR dye onto powdered egg-shell for pseudo-second order kinetic model.](image)

### Table 1. Kinetic parameters for adsorption of Congo red dye onto powdered egg-shell.

| $q_{e,exp}$ (mg/g) | Pseudo-first-order | Pseudo-second-order |
|-------------------|--------------------|---------------------|
|                   | $k_1$ (1/min)      | $q_{e,cal}$ (mg/g)  | $R^2$ | $k_2$ g/(mg·min$^{1/2}$) | $q_{e,cal}$ (mg/g) | $R^2$ |
| 10.05             | -2.07 × 10^{-4}    | 9.71                | 0.7117| 0.065                      | 10.17               | 0.9999 |

**Plausible adsorption mechanism**

Although the kinetic data was found to fit with pseudo-second-order model, it does not provide the idea of adsorption mechanism as well as type of adsorption. To delineate the adsorption mechanism, the kinetic data was further analyzed by using a well-known model, named Weber-Morris intraparticle diffusion model (Cheng et al., 2015).

$$q_t = k_{id} t^{1/2} + C \quad (7)$$

where, $q_t$ (mg/g) is denoted as the adsorption capacity at time $t$ (min), while $k_{id}$ (mg/(g·min$^{1/2}$)) and $C$ are defined as intraparticle diffusion rate constant and boundary layer thickness, respectively. If the Weber-Morris plot is drawn by plotting $q_t$ vs $t^{1/2}$ as shown in Fig. 8, the values of parameters $k_{id}$ and $C$ can be estimated from the slope and intercept of that plot.
However, when the Weber-Morris plot displays a single straight line passing through the origin, particle diffusion would be the rate-controlling step. But when the plot displays more than one linear region, multistage adsorption occurs (Cheng et al., 2015; Parvin et al., 2019a). As depicted in Fig. 8, there are two linear regions where the steeper line is due to the exterior film diffusion, and the second linear region (less steep) is owing to intraparticle diffusion or pore diffusion. However, the intraparticle diffusion rates for those two regions were determined to be $0.0448 \text{mg/(g·min}^{1/2})$ and $0.0074 \text{mg/(g·min}^{1/2})$. A schematic diagram of the adsorption model has been shown in Fig. 9.

**Figure 8.** Weber-Morris plot for adsorption of congo red onto egg-shell powder.

**Figure 9.** Schematic diagram of the adsorption model.

**Adsorption isotherm study**

Adsorption isotherms indicate the relationship between adsorbate (congo red) concentration and its adsorption by the surface of the adsorbent at specified conditions. As a part of this investigation, two different equilibrium isotherm models were applied for further analyzing the obtained equilibrium data. The isotherm models were the Langmuir model and the Freundlich model. And thus, quantification of adsorption capacity was achieved. However, considering the correlation coefficient ($R^2 = 0.4125$), the Freundlich model was not suitable for matching with the found data during experiments. Therefore, the Freundlich model was not discussed in this section; instead, only the Langmuir model was discussed here.
Langmuir isotherm model deals with the assumption that the process of entire adsorption befalls in a monolayer basis, and the adsorption surface is homogeneous. In light of the Eq. 3 if \(1/q_e\) vs \(1/C_e\) is plotted (Fig. 10), a straight line is obtained where a very high correlation coefficient is observed \((R^2 = 0.9912)\). The maximum adsorption capacity \((q_m)\), as well as other adsorption parameters, can be attained from the slope and intercept of the plot. However, the maximum adsorption capacity of egg-shell powder for congo red adsorption as well as the Langmuir isotherm constant was determined, which were 153.85 mg/g and 52.5 L/g, respectively.

![Figure 10. Langmuir isotherm model for adsorption of congo red dye.](image)

Dimensionless separation parameter \((R_L)\) is another essential feature of the Langmuir adsorption isotherm process, which can be stated as follows (Rafatullah et al., 2009):

\[
R_L = \frac{1}{1 + k_L C_i}
\]

where the symbols \(k_L\) and \(C_i\) are considered to be the Langmuir isotherm constant \((L/mg)\) as well as initial adsorbate concentration \((mg/L)\), respectively. The favorability of the isotherm is represented by \(R_L\) value. The adsorption process is favorable if the \(R_L\) value stands between 0 and 1, while it is unfavorable if \(R_L > 1\). The value of \(R_L = 1\) point to a linear adsorption process, while the sorption process is irreversible when \(R_L = 0\). However, the values of dimensionless separation parameters in this study were determined and found to remain within the range of 0 to 1. This signifies that the adsorption process is promising for all the considered concentration.

Conclusion

This research is carried out to find out the potentiality of egg-shell as a low cost and easily available adsorbent for the removal of congo red dye from synthetic wastewater. The influence of the numbers of working parameters such as pH, adsorbent dose, contact time, and initial concentration of dye on the whole adsorption process was evaluated. From the batch-wise adsorption experiment, it is found that maximum adsorption (98.5%) occurred at pH 5, and the optimum time for adsorption was 120 min. The removal efficiency of congo red increases with increasing adsorbent dose, and the equilibrium state was achieved for 1.0 g of egg-shell powder as an adsorbent dose. The obtained data at equilibrium was found to be appropriate with the Langmuir isotherm model elucidating monolayer coverage during the adsorption process. The maximum capacity of adsorption of 153.85 mg/g was found for the studied adsorbent at the tested conditions. The kinetics of adsorption revealed that the kinetic model for pseudo-second-order was best fitted with the data obtained from a series of experiments. From this analysis, it can be decided that the investigated adsorption process can be an alternative technique for eliminating congo red from wastewater.
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