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RESEARCH ARTICLE

REMOVAL OF REACTIVE BLUE 4 (RB4) ONTO PUFFED RICE IN AQUEOUS SOLUTION.

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Abstract

This study deals with the adsorption of Reactive blue 4 (RB-4) dyes onto puffed rice. Batch experiments were performed to evaluate the effects of various experimental parameters like pH, initial concentration, ionic strength and temperatures of dye solutions. The adsorption of RB-4 were found to be most favorable at pH 2, Adsorption of RB-4 followed pseudo-second order kinetics. Calculated activation energy value gives idea about some sort of chemisorption may involve in the adsorption. The value of thermo dynamic parameters shows the adsorption process is endothermic and spontaneous in nature, and three equilibrium isotherm models (Tempkin, Freundlich, Langmuir, isotherm models) were used to analyze the adsorption process. Out of these three models, Langmuir isotherm was found to be best with experimental data for adsorption of RB-4 onto puffed rice. The results indicate that puffed rice is a good adsorbent for the adsorption of RB-4 from wastewater and it is also reusable.

Introduction:-

Textile and dyeing industries are playing important role to make our economy strong but along with that they also creating some environmental problems by discharging colored effluent extensively without proper treatment, which cause pollution in water bodies. Most of which are toxic and non-biodegradable (E. Forgacs, et al., 2004**)**. Dyes can cause allergy, dermatitis, skin irritation (D. S. Brookstein, 2009) and also provoke cancer (R. O. A. de Limaet al., 2007) and mutation in humans (P. A. Carneiro et al.2010). As Reactive Blue 4 (RB- 4) dye is very commonly used in dyeing of cellulosic fabrics (Carneiro et al.2003). The release of this dye into the environment causes huge problem, not only because of their color, but also their breakdown products are toxic and mutagenic to aquatic life. Different kinds of methods are existing for the treatment of textile wastewater with different degree of success (Khan et al.,2011) Amongst these, the removal technique using low-cost adsorbents derived from various natural, agricultural and industrial wastes (Allen et al.,2005) are most widely employed in wastewater treatment. Some agricultural wastes that have been transformed to activated carbon for dye removal are olive kernels (Zabaniotou et al., 2008) Euphorbia rigida (Gercel et al., 2007) bamboo shoot (Hameed, 2009) jute fiber (Senthilkumaar et al., 2006) coconut flower (Padmesh et al., 2005), bamboo dust, coconut shell, groundnut shell, and silk cotton hull for removal of reactive dyes. Researchers are still in search of new adsorbent (N. Mohammad Mahmoodi et al., 2014,A. Hassani et al., 2014,G. Rodney Harris et al., 2006, Banerjee et al., 2014, L. Solomon Bello et al., 2012,Idris et al., 2011,A. Regina Vasques et al., 2009,M. Aseel Aljeboree et al., 2014,M. A. Ahmad et al., 2014,V. Rocher et al., 2008). In this study, puffed rice has been used a adsorbent for the removal of RB-4 from aqueous solution. The kinetic and equilibrium studies were carried out to understand the removal process.

Experimental:-

Materials:-

Puffed rice was collected from local market and was used without further purification although it was grained to make powder. The Reactive Blue 4 (RB4) was obtained from Sigma-Aldrich Germany and was used without purification. The chemical structure of RB4 is shown in Fig: 1. all other reagents and solvents were highest grade of purity. Deionized water was prepared by passing distilled water through a deionizing column (Branstead, Syboron Corporation, Boston. USA).

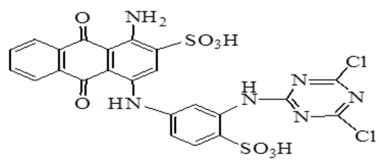

Figure: 1.The chemical structure of RB4.

Characterization:-

Zero point charge (pHZPC) of puffed rice was determined. The FTIR spectra of reactive blue 4 (RB4) and puffed rice before and after RB4 removal were recorded in the frequency range of 400-4000cm-1 using spectrophotometer (IR Prestige-21 FTIR Spectrophotometer, Simadzu, Japan).

Methods:-

Effect of pH:-

Batch sorption studies were carried out by agitating 25 mL of dye solution of the certain concentration (100.13 µmole/L) and 0.1g of the puffed rice powder in 220 mL reagent bottle. Agitation was performed at room temperature (30± 0.20C) with shacking machine at a speed of 120r/min at different time intervals. pH of the solution varied from 2 to 10. The pH of the solutions were adjusted either by adding micro liter quantities of 1 mol/L M HCl or 1 mole/L NaOH. The dye solution was separated from the adsorbent by centrifuging. The dye removal was determined spectrophotometrically (UV-160A, Shimadzu, Japan)) by monitoring absorbance changes at the λmax (595.0 nm) of reactive blue 4 (RB4).

Effect of concentration on the removal process:-

Batch Equilibrium removal of RB4 was investigated under different concentrations ranging 10.50-237.50µmol/L with 0.1g of puffed rice and at 30°C and pH2. The mixture was shaken for 150 min. The dye solution was separated from the adsorbent by centrifuging. The equilibrium concentration of the remaining dye was determined by spectrophotometrically.

Effect of ionic strength on the removal process:-

Batch removal was performed at various ionic strength (0.01M, 0.05M, 0.10M, 0.15M, 0.20M KCl solution) of dye solution (25 ml, 100.13µmol/L) with 0.1g of puffed rice at 30°C and pH2 .The mixture was shaken for 150 min. The dye solution was separated from the adsorbent by centrifuging. The equilibrium concentration of the remaining dye was determined by spectrophotometrically.

Effect of temperature on the removal process:-

Same batch removal method was used at temperatures (30°C35°C40°C45°C) using 100µmol/L of RB4 solution (25ml) and 0.1g of puffed rice at pH2. The mixture were agitated for 150 min. The dye solution was separated from the adsorbent by centrifuging. The equilibrium concentration of the remaining dye was determined by spectrophotometrically.

Isotherm experiments:-

Equilibrium uptake of RB4 was investigated at 30°C, 35°C, 40°C and 45°C with 0.1g of puffed rice in contact with 25ml of RB4 solution of concentration ranging from 50-2000µmol/L at pH2. Agitation time was 150 min. The dye solution was separated from the adsorbent by centrifuging. The equilibrium concentration of the remaining dye was determined by spectrophotometrically.

Desorption experiments:-
Certain concentration (must be in the saturation range) of dye solution was agitated with certain amount of the adsorbent powder for equilibrium time. After shaking the supernatant dye solution was discarded and the adsorbent was separated and allow to wash with deionized water and then dried. For desorption study 0.1g of that was taken in to a shaking bottle with 25ml of 0.1M NaOH solution for 420 min and batch removal process was followed.

Reuse experiments:-
For reuse study 0.1g of the dried and washed residue was taken in to a shaking bottle with 25ml of 1000µm/L of dye solution for 300 min, also maintained pH2 and batch removal process was followed.

Calculations:-
The amount of RB4 adsorbed onto puffed rice q_t (µmole/g) at any time t and q_e (µmole/g) at equilibrium were determined from the following relationships**:-**

$$qt = V(C_0 - C_t)/m \qquad (1)$$

and

$$qe = V(C_0 - C_e)/m \qquad (2)$$

where C_0 (µ mole/L), C_t (µ mole/L), C_e (µ mole/L), are the liquid-phase concentrations of RB4at initial, at any time t, and equilibrium, respectively; V (L) is the volume of RB4solution and m (g) is the amount of dry puffed rice power used.

Results and discussion:-

Determination of point zero charge (pHpzcc):-
The pHPZC of puffed was determined and that was 6. This information help us to understand the behavior of the surface of puffed rice at certain pH such as pH < 6 the surface of the puffed rice will be positively charged whereas pH > 6 the surface of the puffed rice will be negatively charged.

FTIR Analysis:-
In the spectrum of RB4 (Figure is not given) the broad region around 3450.68 cm^{-1} can be assigned to overlapping of OH stretch and -NH functional groups. The peak at 2924.89 and 1654 cm^{-1} (not marked) which corresponds with C-H and C=O stretch, respectively. The band at 1290,89, 1224.13 and 1188.84 cm^{-1} correspond to the S=O stretching, peaks at 796.46 cm^{-1}, 765.20 cm^{-1} for –C-H stretching, 617.94 cm^{-1} –C-Cl stretching.

In the FTIR spectra of puffed rice (Figure is not given) band at 3422.89 cm^{-1} correspond to the O-H and -NH stretching. The band at 2924.28 cm^{-1} correspond to the C-H stretching and band at 854.48cm^{-1} and 762.27cm^{-1} for –NH wagging.

The FTIR spectra of the puffed rice (Figure is not given) after removal of reactive blue 4 (RB4) is shown in. Band at 3422.89 cm^{-1} sifted to 3448.25 cm^{-1} attributed to O-H and N-H stretching, and The band at 1290.89, 1224.13 and 1188.84 cm^{-1} correspond to the S=O stretching in the RB4 FTIR spectrum were absent in FTIR spectrum of puffed rice after removal of RB4.

This analysis concluded that the removal due to the interaction of –OH and –NH groups of puffed rice with $–SO_3^-$ groups of RB4 and some sort of chemisorption may involve in the removal process.

Effect of pH on the removal process:-
The effect of pH on the removal of RB4 by puffed rice was studied in aqueous solution within pH range 2-10. The uptake of RB4 on puffed rice indicated that within 120 min was taken to reach the equilibrium time for all pHs. However the data was taken for 150 min. to make sure that full equilibrium was established. It was observed that the initial rate of removal (h) of RB4 increases significantly with decreasing solution pH. Similar result observed in the removal of acid yellow 36 onto activated carbon prepared from sawdust and rice husk (P.K. Malik, 2003). After 150 min. of removal, the equilibrium sorption capacity (q_e) was found to be 24.55 -3.74 µmol/g at pH 2-10 (Table-1). These results suggest that the initial rate of removal (h) as well as the equilibrium removal capacity of puffed rice is suitable at pH- 2 among the observed pH ranging from 2-10. Experimental results showed the percentage of dye removal increased with decrease in pH of the dye solution.

Effects of initial dye concentration on the removal process:-

It was found that as the initial dye concentration was increased relative to a fixed sorbent dosage, the extent of removal increased (Table:1).At the higher concentration the rate of removal is lower and at lower concentration the rate of removal is higher (Anteneh Worku and Omprakash Sahu. One of the possible reasons for such phenomenon is at lower dye concentration, solute concentrations to adsorbent sites ratio is higher, which cause an increase in color removal and at higher dye concentrations, solute concentrations to adsorbent sites ratio is lower due to the saturation of removal sites, which also results slower rate of color removal. Experimental results showed the percentage of dye removal increased with decrease the concentration of the dye solution.

Effect of ionic strength on dye removal:-

The result is shown in Table-1; it indicates that the higher the KCl concentration is, the lower the removal capacity since the addition of KCl reduces the electrostatic interaction between puffed rice and dye. This agrees with the prediction of the mechanism of electrostatic interactions (R. A. A. Muzzarelli et al., 1973). The addition of salts allows the neutralization of the negative sites of dye molecules which help to lower the attraction force between surface of puffed rice and dye molecule results decrease the removal. Experimental results showed the percentage of dye removal decreased with increase in the ionic strength of the dye solution.

Effect of temperature on removal process:-

Temperature is an important parameter that can influence the equilibrium and rates of sorption processes. When the temperature is raised from 30°C to 45oC, the removal of RB4 onto Puffed rice increased from 24.46 to 24.55 μmole/g, indicating that the process was endothermic and kinetically controlled. This may be attributed to increased penetration of reactive dyes inside microspores at higher temperatures or the creation of new active sites. Similar behavior observed in case of the removal of reactive black C-NN onto manganese-oxides-modified diatomite (MOMD) (M. Al-Ghouti et al., 2005). Experimental results showed the percentage of dye removal increased with increase in the temperature of the dye solution.

Rate Constant Studies:-

In order to find out the mechanism and potential rate-controlling steps involved in the process of removal, pseudo first-order and pseudo second-order and Elovich kinetics models were used. It is found that the experimental all data fitted well to the second-order kinetics than that for the pseudo-first-order kinetics mode and the Elovich Model (Table-1,). Similar results for removal kinetics have also been observed in the case of removal of reactive yellow 2 (RY2) onto activated carbon prepared from cocoa shell.

Adsorption mechanism:-

To determine the rate limiting step and corresponding rate constants, the kinetic data were further processed by the intraparticle and film diffusion models. The intraparticle diffusion model equation proposed by Weber and Moris and film diffusion model equation proposed by McKay were used.

The values of diffusion kinetic parameters (k_{id} and k_f) and R2 obtained from applied and it can be seen none of the linear plots at any concentration pass through the origin (Figures are not shown) which means both intraparticle diffusion and film diffusion may involve in the rate limiting steps of the removal onto puffed rice. Similar result observed in the removal of congo red from effluents of the textile industry using rice husk carbon activated by steam(J. Sharma and B. Janveja, 2008).

Activation Energy of the removal process:-

The activation energy (E_a) for the sorption RB4 dye on puffed rice can be estimated by using Arhenius equation (3).

$$lnk = lnk_0 - \frac{E_a}{RT} \quad (3)$$

In this work, activation energy of sorption process has been calculated using the values of rate constant (k_2) from a pseudo-second-order kinetic equation and using the appropriate solution temperatures (Table-1). When lnk2 is plotted versus 1/T (Figure is not given), a straight line with slope ($-E_a/R$) is obtained).

Low activation energies (5–40 kJ/mole) are characteristics for physisorption, while higher activation energies (40–800 kJ/mole) suggest chemisorption .The values of E_a from the slopes of the plots is 69.13 kJ/mole for RB4 dye. Which indicating the rate-limiting step in the removal process, might be a chemically controlled type (Mi-Hwa Baek et al., 2010**)**. To calculate the thermodynamic parameters such as enthalpy of activation ($\Delta H^{\dagger}$), entropy of activation ($\Delta S^{\dagger}$) and free energy of activation ($\Delta G^{\dagger}$) the equation (4) was used.

$$\mathbf{\ln(k_2 /T) = -\Delta H^{\dagger} /R(1/T) + \ln (k_B /h_p) + \Delta S^{\dagger}} \qquad (4)$$

The slope and y-intercept of the plot $\ln(k_2 /T)$ versus 1/T (Figure is not given). The value of $\Delta H^{\dagger}$ was found to be 71.71 kJ/mole, which is consistent with endothermic nature of the diffusion process. The value of $\Delta S^{\dagger}$ was estimated to be 174.41 J/mole K, which reflects significant change occurs in the internal structure of the absorbent material during removal. The positive value of $\Delta G^{\dagger}$ indicate the presence of an energy barrier in the removal process which is supported by many previous work.

Table: 1**:-** Comparison of calculated and experimental q_e values and kinetic parameters for the RB4 adsorption onto puffed rice at various pHs, initial concentrations of RB4, ionic strength and temperatures

Parameters	qe(exp.) (µmol/g)	Pseudo-first-order kinetic			Pseudo-second-order kinetic				Elovich kinetic model		
		k1 (min-1)	q_e (cal.) (µmol/g)	R^2	k_2 (g/µmol/ min)	q_e (cal.) (µmol/ g)	h (µmol/g/ min)	R^2	α (µmole/g/min)	β (g/mole)	R^2
pH	Initial Concentration of RB4 solution 100.13µmol/L.										
2	24.55	0.0601	10.24	0.952	0.0145	25.13	9.15	0.999	3.16E+02	0.37	0.897
3	23.09	0.0304	8.78	0.905	0.0091	23.75	5.13	0.999	2.04E+01	0.26	0.857
4	21.37	0.0200	9.14	0.961	0.0060	22.03	2.93	0.995	7.24E+01	0.40	0.982
5	18.69	0.0189	8.49	0.972	0.0060	19.34	2.26	0.994	4.17E+01	0.43	0.967
6	14.21	0.0173	5.53	0.950	0.0097	14.56	2.05	0.994	8.13E+01	0.65	0.973
7	8.82	0.0603	5.32	0.991	0.0235	9.17	1.97	0.999	1.07E+01	0.73	0.912
8	7.04	0.0742	9.43	0.975	0.0102	8.83	0.80	0.995	3.51E+00	0.70	0.992
9	5.36	0.0244	3.41	0.978	0.0140	5.74	0.46	0.995	1.75E+00	1.03	0.996
10	3.74	0.0281	3.07	0.971	0.0135	4.15	0.23	0.988	1.24E+00	1.40	0.957
IniInitial RB4 Concentration (µmole/L)(pH-2)											
10.50	2.59	0.0260	2.78	0.955	0.0621	2.64	0.43	0.999	3.2E+01	3.87	0.982
51.13	12.37	0.0281	1.38	0.910	0.0719	12.41	11.06	0.999	2.6E+09	2.19	0.905
100.13	24.08	0.0613	8.72	0.958	0.0187	24.51	11.21	0.999	4.1E+02	0.39	0.883
151.25	36.20	0.0348	11.52	0.985	0.0083	36.90	11.26	0.999	9.8E+02	0.28	0.970
199.38	44.21	0.0433	19.28	0.964	0.0056	45.45	11.49	0.999	1.8E+02	0.18	0.954
237.50	49.13	0.0283	16.95	0.860	0.0046	50.25	11.72	0.999	1.9E+02	0.16	0.951
Ionic Strength (mole/L), Initial Concentration of RB4 solution 101.50µmol/L.l(pH-2)											
0.01	24.91	0.0603	2.97	0.955	0.0758	25.00	47.39	0.999	2.9E+10	1.14	0.829
0.05	24.88	0.0537	3.01	0.952	0.0632	25.00	39.53	0.999	3.2E+06	0.88	0.838
0.10	24.81	0.0567	3.50	0.891	0.0596	24.39	35.46	0.999	3.2E+06	0.76	0.826
0.15	24.68	0.0567	2.66	0.835	0.0582	24.81	35.84	0.999	1.5E+06	0.73	0.882
0.20	24.61	0.0797	5.79	0.968	0.0481	24.81	29.59	0.999	1.5E+06	0.68	0.882
Temperature (0C Initial Concentration of RB4 solution 100.00µmol/L.),(pH-2)											
30	24.46	0.0564	4.44	0.895	0.0392	24.63	23.81	0.999	1.4E+05	0.64	0.789
35	24.49	0.0495	2.75	0.860	0.0578	24.63	35.09	0.999	9.3E+07	0.92	0.769
40	24.52	0.0410	1.6	0.405	0.0937	24.63	56.82	0.999	1.8E+09	1.04	0.713
45	24.55	0.0463	1.28	0.321	0.1409	24.63	85.47	0.999	9.4E+10	1.20	0.649

Adsorption isotherms:-

Adsorption isotherm of RB4 dye on puffed rice at various temperatures was made by plotting equilibrium removal capacity (q_e) of puffed rice versus equilibrium concentration of dye in aqueous phase (C_e). It shows removal capacity increases with increasing temperature. This observation approves with the temperature effect. The rise in removal capacity is due to the increase in collision frequency between adsorbent and adsorbate, which results in the greater removal onto the surface of the adsorbent. This improvement may be due to the creation of new reaction sites or increased rate of inparticle diffusion of adsorbate molecules into the pores of the adsorbent at higher temperature. Various isotherm equations such as Tempkin, Freundlich and Langmuir were used to calculate the values of various constants. All the experimental values are listed in Table: 2.

Table: 2. Freundlich, Tempkin and Langmuir isotherm constants at different temperatures and thermodynamic parameters for the adsorption of RB4 onto puffed rice from aqueous solution at pH 2

Isotherms	Parameters			
Tempkin				
Temperature (°C)	30	35	40	45
K_T (µmole/L)	826.24	301.43	194.80	124.08
b_T (J/mole)	690.35	603.06	531.99	450.05
R^2	0.931	0.943	0.920	0.893
Freundlich				
K_F ((µmol/g)(µmol/L)$^{-1/n}$)	24.82	24.80	25.94	27.85
b_F (J/mole)	0.10	0.11	0.12	0.14
n	9.83	8.85	8.16	7.35
R^2	0.907	0.922	0.889	0.848
Langmuir				
K_L (L/g)	7.50	8.26	10.81	13.21
a_L (µmole/L)	0.15	0.16	0.18	0.19
q_m (µmole/g)	49.50	53.19	58.82	67.57
R_L	0.00007	0.00006	0.00005	0.00004
R^2	0.999	0.999	0.999	0.999
Thermodynamic Parameters				
Temperature (K)	303	308	313	318
ΔG (kJ/mole)	-30.05	-30.61	-31.54	-32.16
ΔH (kJ/mole)	13.98			
ΔS(J/mole/K)	145.15			
R^2	0.999			

Which shows that the Langmuir removal isotherm provides a good explanation of data for RB4 dye over the whole temperature range studied in single systems since R^2 values from Langmuir isotherms (Table-2) are always greater than that of Freundlich isotherms (Table-2) and Tempkin isotherm (Table-2). Similar result observed in the removal of methylene blue onto sunflower seed husk (Siew-Teng Ong et al., 2010). Thus, it can be concluded that monolayer removal is occurred in this study. Thus, the equilibrium constants or binding constants (a_L) obtained from Langmuir isotherms are used to calculate the thermodynamic parameters for the removal process.

Thermodynamic parameters:-

Van't Hoff equation were used to calculate the values of ΔG ΔH and. ΔS. From the slope and y-intercept of Van't Hoff plot of $\ln a_L$ vs. 1/T (Figure is not shown). Generally a value of ΔH in between 5-40 kJ/mol is consistent with electrostatic interaction between removal sites and adsorbing ion (physical removal) while a value ranging from 40-800 kJ/mol suggests chemisorption (M.Dogan, Alkan et al., 2006).

The values of ΔH and ΔS are presented in Table: 2. The results show that the changes in enthalpy, ΔH for the removal of RB4 by puffed rice were 13.98 kJ/mol. A positive enthalpy change, ΔH suggests that the interaction of dye adsorbed by puffed rice is endothermic which is supported by the increasing removal of the dye with the increasing in temperature while a negative removal standard free energy change (ΔG) indicate that the removal reaction is a spontaneous process. The positive value of ΔS also indicates that the randomness increases at the solid--solution interface during the removal of dye onto the puffed rice.

Desorption studies:-

Desorption study showed that RB4 desorbs in alkaline solution which suggests the ion exchange mechanism involved in the removal it also indicates the chemisorption also take part in the removal process (Fig: 2).

Reuse:-

This step is performed to test the feasibility of puffed rice as a reusable adsorbent. It is found that puffed rice can be used as a reusable adsorbent (Fig: 2).

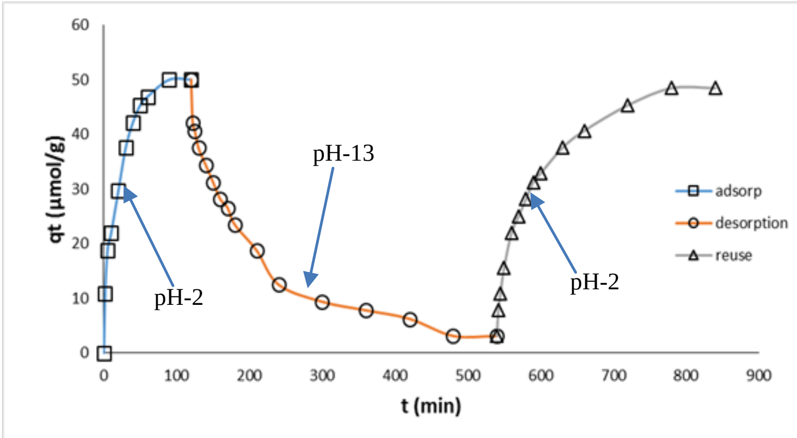

Figure: 2. Adsorption-Desorption-Reuse Cycle

Conclusion:-

The present study shows that the puffed rice is an effective adsorbent for the removal of RB-4 from aqueous solution. The removal of RB4 is maximum at pH2. The kinetics of RB-4 confirms that removal followed second-order rate expression and demonstrated that intra particle diffusion and film diffusion plays a significant role in the removal of RB-4. However, from the comparison of the removal isotherms it can be seen that removal experimental data for RB-4 onto puffed rice were best represented by the Langmuir isotherm model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the outer surface of the adsorbent. Thermodynamic parameters shows that the removal process is endothermic in nature and spontaneous. Both chemical and physical removal involved in the process. Desorption shows that the removal process is chemisorption type and ion exchange mechanism is also takes part in removal process. Reuse study indicated that the puffed rice is reusable adsorbent and capable for the removal of RB-4 with high affinity and capacity.

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