



Equilibrium Sorption studies of Fe, Cu and Co ions in aqueous medium using activated Carbon prepared from *Recinius Communis Linn.*

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ABSTRACT: *Recinius Communis Linn* a commonly found herbal plant was used to prepare activated carbon by physicochemical activation method. The sorption capacity of this bio-resource material to remove Fe(III), Cu(II) and Co(II) from aqueous solutions was determined by batch tests. The influences of important parameters such as contact time, dosage, pH, pH zpc, co-ions and temperature on metal adsorption process were investigated. The equilibrium data were fitted to Langmuir and Freundlich isotherms. The batch adsorption rate for the sorption process was explained on the basis of intraparticle diffusion. Various thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 were analyzed to observe the nature of adsorption. The metal adsorption process on the surface of adsorbent was verified as a surface phenomenon by performing SEM and XRD analysis. @ JASEM

Metals can be distinguished from other toxic pollutants, since they are not biodegradable and can be accumulated in living tissues, causing various diseases and disorders. Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, ion exchange, reverse osmosis, ultra filtration, biological systems and adsorption (Gode and Pehlivan, 2005) Adsorption processes for removal of metals have been found cheaper and more effective than the several technologies. (Gupta et al., 2003) Numerous by products of agro – industrial productions and agricultural by – products have been studied for potential use as inexpensive sorbents. (Ho, 2003) Many examples are available in the literature concerning the direct or activated use of these materials as adsorbents. (Cochrane et al, 2006; Bailey et al, 1999; Abia et al, 2002) This study deals with the investigation of Fe(III), Cu(II) and Co(II) removal from aqueous solutions by adsorption on activated carbon prepared from *Recinius Communis Linn* (RC).

MATERIALS AND METHODS

The preparation of activated carbon from RC consisted of carbonization of the plant material. Dried raw leaves were cut into small pieces and the carbonization was conducted in a muffle furnace at 400°C. The heating period was 2 hours. After

carbonization, the carbon was ground using domestic mixie. The activated carbon obtained was kept in a desiccator and were characterized for the physical parameters which are given in **Table 1**. Adsorption equilibrium study of these metal ions was carried out in 250ml stoppered Iodine flask. The concentration of the metal ions was determined by UV/ Visible spectrophotometer (UV 240 Shimaduzu). All other water quality parameters were analyzed by using standard methods (APHA, 1998). The pH measurements were done with a pH electrode (Systronics) and pH_{ZPC} (pH of zero point charge) was determined by pH drift method. (Jia et al, 2002) The surface morphology of the raw and treated activated carbons was visualized by SEM with a HITACHI-S-3000H model. XRD pattern was recorded using X¹ per PRO (model), PAN analytical (make). Computations were made using Microcal Origin, (version 6.0) software.

Table 1. Characteristics of the activated carbon

S.No	Parameters	Recinius Communis Linn
1	Particle size (mm)	0.15
2	Density (g/cc)	0.54
3	Ash content (%)	2.04
4	Moisture content (%)	1.64
5	Loss of ignition (%)	82.0
6	Water soluble matter	0.17
7	pH of aqueous solution	7.5
8	pH (zpc)	7.1
9	Iodine number (mg/g)	204

Table 2. Langmuir and Freundlich constants

Metal ions	Temperature	Langmuir constants			Freundlich constants			
		Q ₀	b	R ²	R _L	1/n	K _r	R ²
Fe(III)	303	1.546	0.304	0.998	0.910	0.743	3.526	0.997
	313	1.557	0.3621	0.999	0.976	0.750	3.718	0.998
	323	1.569	0.4031	0.999	0.905	0.757	3.996	0.998
	303	1.181	0.157	0.999	0.968	0.742	3.554	0.998
Cu(II)	313	1.188	0.164	0.999	0.968	0.746	3.705	0.998
	323	1.194	0.180	0.999	0.965	0.754	3.967	0.999
Co(II)	303	1.574	0.132	0.997	0.815	0.887	3.071	0.999
	313	1.636	0.159	0.998	0.834	0.836	3.264	0.999
	323	1.762	0.168	0.999	0.853	0.811	3.697	0.999

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RESULTS AND DISCUSSION

The effect of time on the adsorption of metal ions by RC for iron(III), copper(II) and cobalt(II) with 50ml of 20 ppm of each metal ion solutions were studied. Fig.1 shows the effect of contact time on adsorption of the adsorbent. The effect of the activated carbon RC dose on the removal of metal ions is shown in fig.2. The adsorption increased from 45 to 90 percentages with increase in adsorbent dose from 50 mg to 500mg. The pH dependence of iron(III), copper(II) and cobalt(II) take onto RC is shown in fig.3. It is well known that these metal ions undergo hydrolysis reactions in water and form insoluble complexes with increasing pH. (James and Healy, 1972) This phenomenon is conceded as important for understanding the adsorption behaviour of all metal ions onto these activated carbons. Up to pH 5.0 due to the presence of H^+ ions of the acid used for adjusting pH. However, this effect causes in the pH range of 5.0-7.0. (Celik et al, 1995) The influence of other co-ions such as Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , Ca^{2+} , and Mg^{2+} which are commonly present in water, on the adsorption of iron(III), copper(II) and cobalt(II) by the activated carbon was investigated. Fig. 4 gives the effect of co-ions on the adsorption of copper(II) as representative plot. In all the cases, the presence of these co-ions did not significantly alter the metal ions adsorption process by the activated carbon. Equilibrium data are basic requirements for the

design of adsorption systems and adsorption models are used for the mathematical description of the adsorption equilibrium of the metal ions on to the adsorbent. The results obtained on the adsorption of iron(III), copper(II) and cobalt(II) were analyzed by the well – known models given by Langmuir and Freundlich.

Langmuir isotherm. The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e, \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption. The Langmuir curves pertaining to the Cu(II) adsorption by RC is provided in fig.5 as representative plot. The Langmuir constants b and Q_0 were calculated from equation (2) and the values are given in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which is defined by,

$$R_L = \frac{1}{1 + bC_0}, \quad (2)$$

where b is the Langmuir constant and C_0 is the initial concentration (mg/L). The value of R_L indicates the type of the isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$)

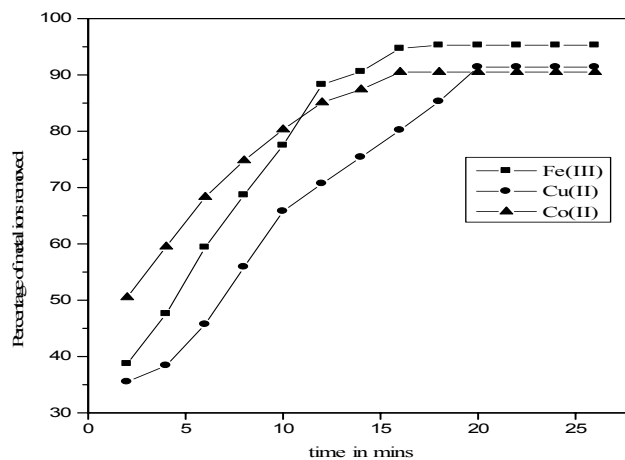


Fig. 1. Effect of contact time for RC

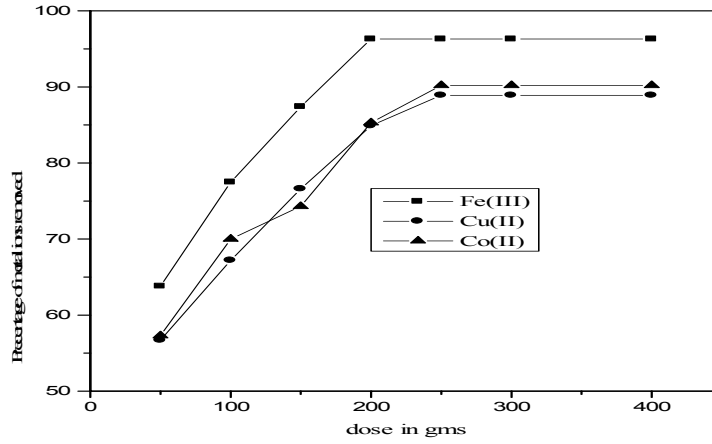


Fig. 2. Effect of dose for RC

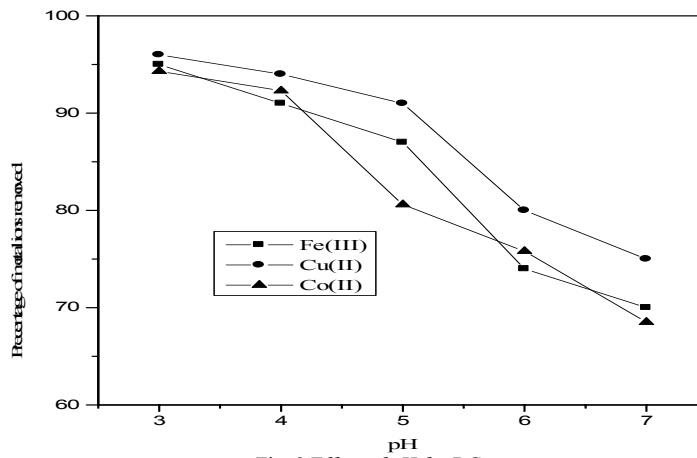


Fig. 3 Effect of pH for RC

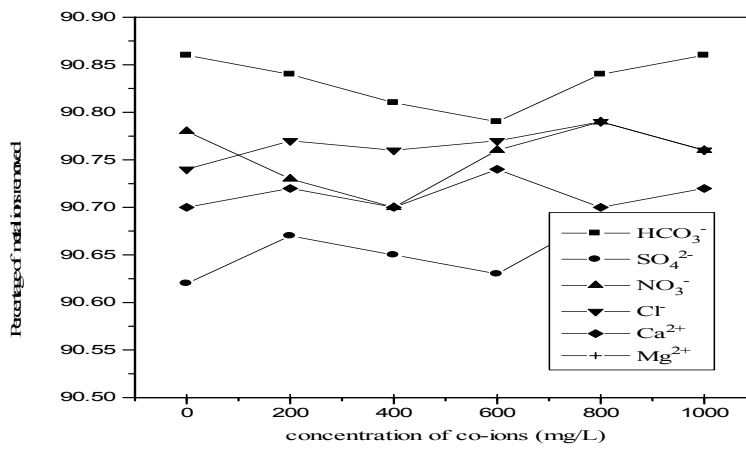


Fig. 4. Effect of co-ions

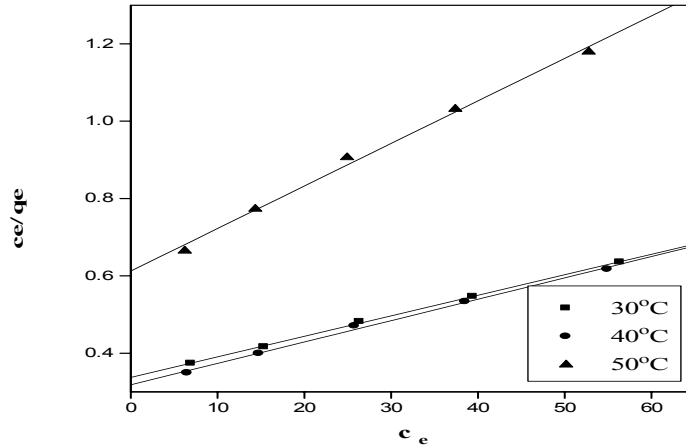


Fig. 5. Langmuir plot of RC

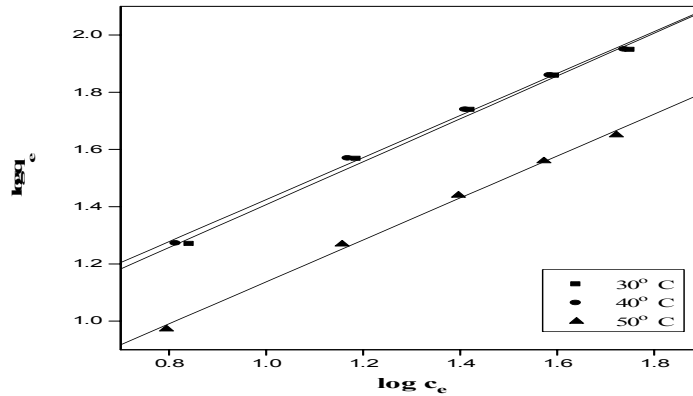


Fig. 6. Freundlich plot for RC

(Mor et al, 2007). The value of R_L was found to be less than one and this again confirmed that the Langmuir isotherm model was favourable for adsorption of metal ions onto the activated carbon under the conditions used in this study. Freundlich isotherm The well-known logarithmic form of Freundlich isotherm is given by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_f and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The values of K_f and $1/n$ were obtained from the slope

and intercept of the plot of $\log q_e$ versus $\log C_e$. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. (Raji and Anirudhan, 1997) Freundlich constants K_f and n values were calculated and listed in **Table 2** and the plot is given in **fig.6**. Thermodynamic parameters with the adsorption viz., standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the equation below and the values are given in **Table 3**.

Table 3.
parameters for
ions at 20 ppm

Metals	$\Delta G^0 (KJ m o l^{-1})$			$\Delta H^0 (KJ m o l^{-1})$	$\Delta S^0 (KJ m o l^{-1})$
	303K	313K	323K		
Fe(III)	-2.50	-2.68	-2.94	+5.25	0.059
Cu(II)	-2.44	-2.26	-2.70	+4.89	0.073
Co(II)	-1.66	-1.26	-1.70	+9.57	0.084

Thermodynamic
sorption of metal

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$$\Delta G^{\circ} = -RT \ln K_o, \quad (4)$$

where the ΔG° is the free energy of adsorption, T is the temperature and R the Universal gas constant. The adsorption distribution coefficient K_o for the adsorption reaction was determined from the slope of the plot $\ln(q_e / c_e)$ against C_e at different temperature and extrapolating to zero C_e according to method suggested by Khan and Singh. (Khan and Singh, 1987) The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature,

$$\ln K_o = \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}, \quad (5)$$

Where the values of ΔH° and ΔS° can be obtained from the slope and intercept of the plot of $\ln K_o$ against $1/T$. (Meenakshi and Viswanathan, 2007) From a mechanistic point of view, to interpret the

experimental data, production of the rate-limiting step is an important factor to be considered in the sorption process. Though kinetic and equilibrium isotherm studies help to identify the adsorption process, predicting the mechanisms is required for design purpose. For a solid - liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. This is determined by plots of the amount of metal adsorbed against the square root of time, $t^{1/2}$ for three different temperatures. According to Weber, an intraparticle diffusion coefficient is defined by the equation.

$$q_t = K_p t^{1/2}, \quad (6)$$

q_t = the amount of metal ions adsorbed per unit mass of adsorbents at any time t

$t^{1/2}$ = square root of time

K_p = Intraparticle diffusion rate constant

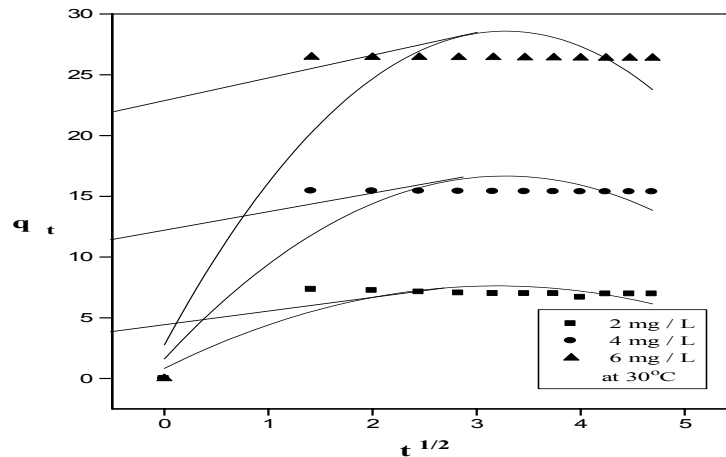


Fig. 7. Effect of intraparticle diffusion for RC

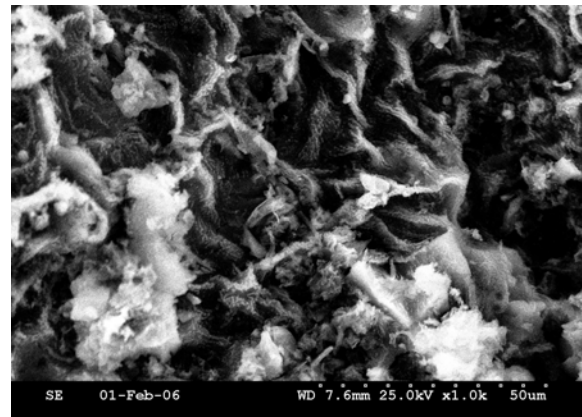
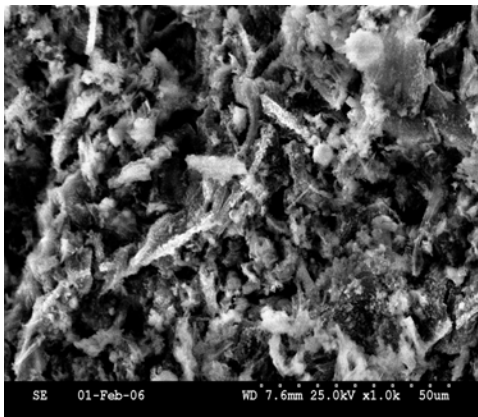


Fig. 8. a) SEM for RC before treatment b) SEM for RC after treatment

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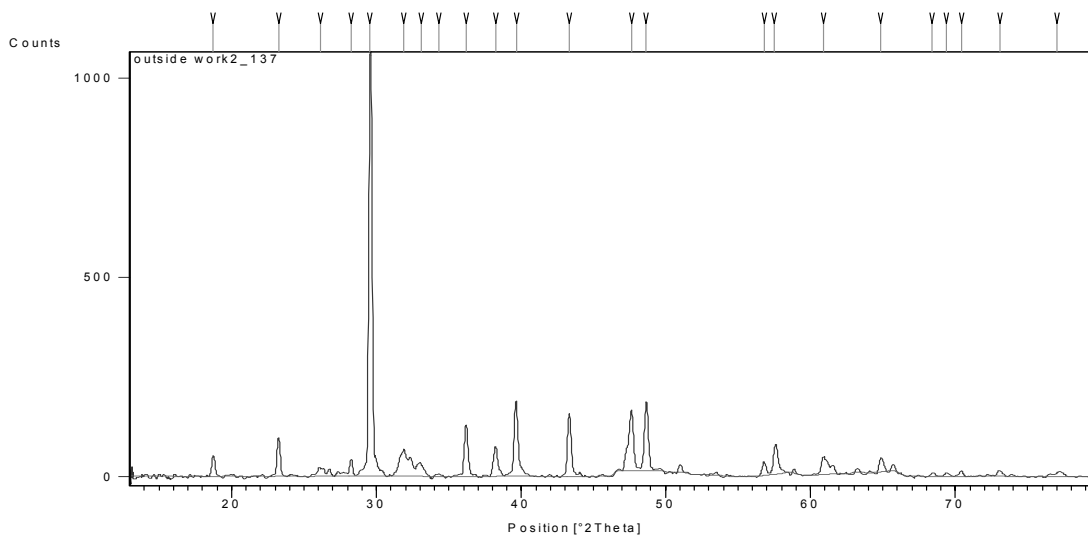


Fig.9 a) XRD for RC before treatment

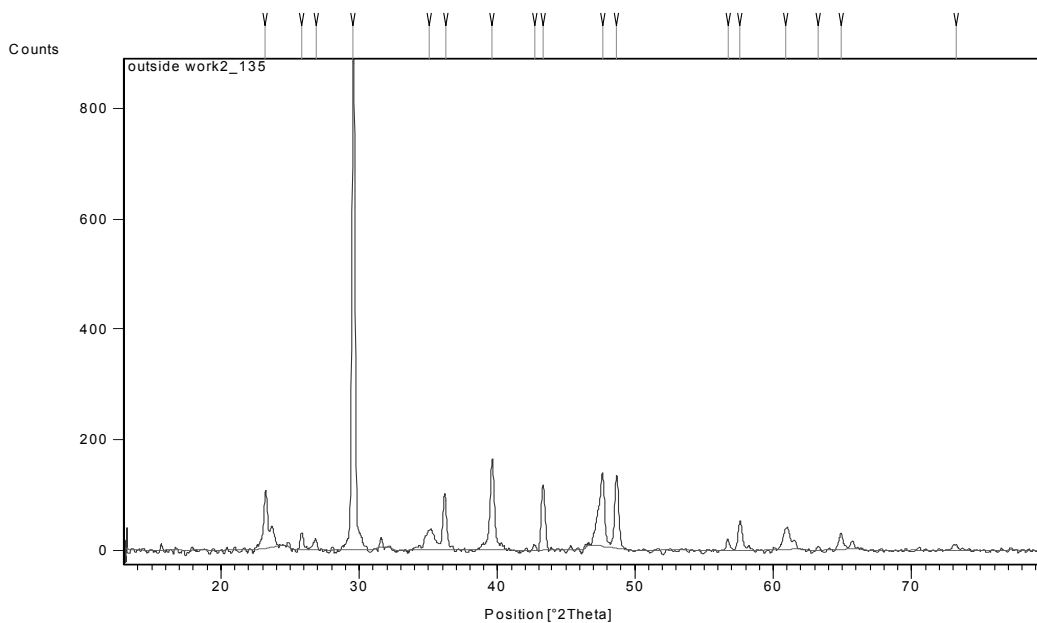


Fig.9 b) XRD for RC after treatment

The plots of intraparticle diffusion curves shows initial curved portion followed by linear portion and a plateau. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption where the intraparticle diffusion is rate controlled. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentration in solutions. (Chenung et al, 2007) Fig.7 shows Cu(II) adsorption by RC as representative plot. SEM images of the activated carbon before and after of iron(III) sorption are shown in fig.8 above as representative images.

Comparison of these micro graphs before and after iron(III) sorption shows that there adsorption of metal ions on the surface of the activated carbon. XRD patterns of the treated adsorbents showed significant changes. The XRD data of the treated activated carbon provided evidence of decrease in the peak intensity at 2Θ values which shows that adsorption of iron(III) on the surface of the adsorbent and at the same it dose not alter the crystalline structure of the material. (Gopal and Elango, 2007) Fig. 9 above indicate the decrease in the peak intensity values after adsorption of RC, on iron(III) as representative.

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