Research Article

Development of Low Cost Adsorbent from Cow Horn for the Biosorption of Mn (II), Ni (II) and Cd (II) Ion from Aqueous Solution

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Abstract: Development of low cost adsorbent from cow horn for the biosorption of Mn (II), Ni (II) and Cd (II) ion aqueous solution was carried out by batch adsorption experiment at 32°C. Parameters such as pH, contact time, metal ion concentrations as well as temperature were monitored. The residual concentration of Mn (II), Ni (II) and Cd (II) were determined using Atomic Absorption Spectrophotometer. The results revealed that maximum Ni (II) and Cd (II) ion removal occurred at pH of 6 while Mn (II) ion occurred at pH of 7 respectively. Langmuir and Temkin adsorption isotherm were used to describe the equilibrium data. The equilibrium data fitted well to Langmuir isotherm than Temkin isotherm. Thermodynamic investigation showed that standard Gibbs free energy (ΔG°) was positive indicating the feasibility and non-spontaneous of the process. The positive value of standard Enthalpy (ΔH°) implies that the reaction was endothermic and the negative standard Entropy (ΔS°) signifies decrease in the randomness at the solid/solution interface of the adsorbent during the adsorption process. The kinetic study revealed that adsorption of Mn (II), Ni (II) and Cd (II) could be best described by pseudo-second model. This study demonstrated that adsorbent developed from cow horn could be used as an alternative to commercial activated carbon in the removal of Mn (II), Ni (II) and Cd (II) ions from aqueous solution.

Keywords: Aqueous solution, bio sorption, cow horn, isotherm, metal ions, thermodynamics

INTRODUCTION

The increase discharge of industrial effluents containing potentially toxic elements into environments through anthropogenic activities has become a matter of apprehension over the years. This could be attributed to the tremendous increase in industrialization and urbanization which simultaneously posed a great threat globally (Hanan et al., 2010). Apart from organic pollutants that were prone to biological degradation, potentially toxic elements do not degrade into harmless end product but tends to build up in living organisms causing diverse diseases (Yu, 2005). The presence of these potentially toxic elements in significant quantities in aquatic environment is known to cause severe damage to aquatic life and human health (Omotoso et al., 2010). As a result of these, the treatment of polluted industrial effluent before being discharged into the environment should be considered as a matter of urgency. Nickel is one of the potentially toxic elements that are not bio-degradable in nature. Due to frequent handling of nickel in developing countries during industrial process, their fume is release

into the atmosphere and may also be discharge into water bodies. The high concentration is toxic to human and can cause gastro intestinal irritation. Ni (ii) ion is a chronic toxic metal ion that can cause cancer of the lungs, nose and bones (Nwabanne and Igbokwe, 2008). Cadmium is an extremely toxic element and its exposure may results to flu like symptoms including chills, fever and muscle ache sometimes referred to as "cadmium blues" which may results to respiratory damage after few weeks. More intense exposures causes tracheo-bronchitis, pneumonitis, diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly infertility. According to whose recommendation Cd (II) limit in drinking water is 0.005 mg/L and above this level may course serious infection (Lenntech, 2011).

However, exposure to manganese at high concentration and consumption of manganese contaminated food also pose serious health challenges which include nerve damage, weak muscles, dullness, lungs embolism and bronchitis, forgetfulness and low Intelligent Quotient (IQ) of children (Maryse, 2010).

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Therefore, adequate measure should be in place to reduce the pollution caused by these elements in order to minimize the health effects (Nadeem et al., 2009). Considering the latent hazard posed on marine life, agricultural product and human life, many methods of remediation have been designed which includes precipitation, membrane filtration, solvent extraction and electro-dialysis, chemical precipitation, electroflotation, ion exchange, reverse osmosis and membrane filtration (Nouri et al., 2008). Most of these methods are costly, inadequate efficiencies mostly at low metal ion concentration especially in the range of 1-100 mg/L (Hossam and Akasha, 2007). Apart from these, activated carbon produced by carbonizing organic materials were also used but the high cost of activating process restricts its usage in waste water treatment (Gaikward, 2004). However, bio-sorption appeared as an ideal substitute compared to the earlier mentioned techniques as a result of the availability of the adsorbent at little or no cost, its affordability, environmental friendliness and high adsorptive capacity (Moshen, 2007). These features make the process of adsorption more economical and effective than the use of commercial activated carbon. In addition, large quantities of cow horn are being released on daily bases in Pata abattoir, Minna. They are under utilized and as such constitute environmental nuisance due to lack of proper solid waste disposal method. Due to this, the present research study attempt to use cow horn as an adsorbent material to remove Cd (II), Mn (II) and Ni (II) ions from aqueous solution.

MATERIALS AND METHODS

Sample collection and preparation: The cow horns were randomly collected at Pata Abattoir in Minna Metropolis, Niger state. The cow horns were washed thoroughly with detergent and rinsed with de-ionized water to remove the debris, sun dried for some months, after which grounded to powder form with mortar and pestle. The grounded were sieved using 300 and 350 μ m mesh size. The sample retained on 350 μ m was then used for sorption studies.

Sample pre-treatment: The fine powder was then soaked in chloroform for 72 h to remove the fat, after which it was sun dried and washed with de-ionized water to remove the color. The fine powder was then modified with $1M \text{ HNO}_3$ for 6 h so as to increase its binding capacity and after which it was washed with de-ionized water and sun dried.

Preparation of metal ion concentration: All chemicals used in this research study were of analytical reagent

grade and were used without further purification. The stock solution was prepared by dissolving 2.76, 4.02 and 4.06 g of Cadmium Nitrate Cd (NO₃) 2.4 H₂O, Nickel Chloride (NiCl₂.6H₂O) and Manganese Sulphate MnSO₄.4 H₂O respectively in 1000 cm³ and diluted with de-ionized water to mark. This gave a concentration of 1000 ppm. One hundred ppm was further prepared from the 1000 ppm stock. The different concentrations of 5, 10, 20, 30, 40 and 50 ppm was prepared from 100 ppm by serial dilution for further experiment.

Sorption experiment:

Effect of pH: (0.5 g) of the adsorbent was added to 30 cm³ of the aqueous solution of 5 mg/L at different pH of 1-8 in a conical flask. The pH of the solution was adjusted to desired value using 1M HCl or 1M NaOH solution. The resultant solution with the adsorbent in the flask was corked and agitated on a multipurpose shaker for period of 60 min, after which the mixtures were filtered. The residual filtrate was analyzed using Atomic Absorption Spectrophotometer (Perkin Elmer, Analyst 200).

Effect of contact time: (0.5 g) of the adsorbent was added to 30 cm³ aqueous solutions of 5 mg/L. The mixture was shaken constantly on a multipurpose shaker at 300 rpm speed for the time period of 20, 40, 60, 80, 100 and 120 min, respectively. At the end of each contact time, the mixture was filtered and the residual concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (AAS), (Perkin Elmer, Analyst 200).

The effect of initial metal ions concentration: (0.5 g) of the adsorbent was added to 30 cm³ aqueous solution of initial metal ion concentration of 10, 20, 30, 40 and 50 mg/L. The mixture was agitated constantly using a multipurpose shaker at 300 rpm speed for 60 min for the three metal ions of concern. At the end of each contact time, the solution was filtered and the residual concentration was analyzed using Atomic Adsorption Spectrophotometer.

The effect of temperature: The batch adsorption process was studied at different temperature of 20 to 100° C in order to investigate the effect of temperature on the adsorption process. This was done by contacting 0.5 g of cow horn with 30 cm³ of 10 mg/L of metal ion solution at the optimal pH. The mixture was place in a water bath and agitated for 60 min. At the end of each temperature, the mixture was filtered and the residual metal ion was analyzed using Atomic Absorption Spectrophotometer (Perkin Elmer, Analyst 200).

DATA ANALYSIS

The percent metal ions removed from solution were calculated by the following equation:

$$D/D = C_0 - C_1 / C_0 \times 100$$
(1)

where,

 C_0 = Initial concentration of heavy metal C_1 = Final concentration of heavy metal

The adsorption capacity q_e was calculated by mass balance relationship equation shown below:

$$q_e = (C_0 - C_1) \times V/m \tag{2}$$

where,

V = The volume of the solution m = The mass of adsorbent (g)

Langmuir isotherm: The Langmuir isotherm is usually expressed as:

$$q_e = (q_{max} C_e) / (K_L + C_e)$$
 (3)

where,

- q_e = The equilibrium value of amount of metal ions adsorbed per unit weight of adsorbent (mg/g)
- q_{max} = The maximum uptake level corresponding to monomolecular layer coverage (mg/g)
- C_e = The equilibrium concentration of the adsorbate
- k_L = The Langmuir's constant (L/mg). Equation (2) was obtained which could be used for correlation purposes:

$$C_e/q_e = (1/k_L.q_{max}) + (1/q_{max}) .C_e$$
 (4)

Equation (2) can be interchangeably used $(1/k_L.q_{max})$ and $(1/q_{max})$.

From the above relation q_{max} and k_L can be calculated. The favorability of an adsorption process or adsorption isotherm is depended on the dimensionless constant factor R_L , which could be obtained as:

$$RL = 1/1 + KL.C_0$$
 (5)

 C_o = The initial metal ion concentration If RL = 0, it shows that the adsorption isotherm is irreversible and if 0<RL<1 then it shows that Langmuir adsorption isotherm is favorable (Patel and Suresh, 2008). If RL = 1 and RL>1 then it is linear. **Temkin adsorption isotherm:** This model was suggested by Temkin and Pyzhev (1940) which described an equal distribution of binding energies over the number of exchanging sites on the adsorbent surface. During the process of adsorption, there is equivalent distribution of maximum binding energy. The decline in the heat of adsorption is not logarithmic but linear which can be expressed as follows:

$$Qe = a + b \ln C_e \tag{6}$$

where,

Qe = The amount adsorbed at equilibrium

- C_e = The equilibrium concentration of the metal ions in the solution (mg/L)
- a = The equilibrium binding constant
- b = Corresponding to the heat of adsorption, both a and b are slope and intercept respectively

Adsorption kinetics: The progress of the adsorption method was monitored by measuring the number of particles adsorbed per unit time (Demirbas, 2007). Various kinetic models have been suggested for the adsorption of solutes on solids. This research study makes use of Lagergrens pseudo-first and pseudosecond order model.

This model could be expressed as follows:

$$dQt = k_1 (Q_e - Q_t) / dt$$
(7)

where, Q_e and Q_t are the adsorption capacity at equilibrium at time t respectively (mg/g).

K1 is the rate constant of pseudo-first order adsorption (min⁻¹). After integration, t = 0 to t = t and $Q_t = 0$ to $Q_t = Q_t$, the integrated form of this equation becomes:

$$\ln \left(\mathbf{Q}_{e} - \mathbf{Q}_{t} \right) = \ln \left(\mathbf{Q}_{e} \right) - \mathbf{K}_{1} \mathbf{t}$$
(8)

The equation above is confirmed if graph of log (Q_e-Q_t) against (t) is a straight line. Where K_1 and Q_t are slope and intercept respectively:

$$\log \left[q_{e} / (q_{0} - q_{t}) \right] = K_{1} / 2.303t \tag{9}$$

rearranged to obtain a linear form:

$$\log (q_e - q_t) = \log q_e - K_1 / 2.303$$
(10)

Pseudo-second-order model: The pseudo second order adsorption kinetic rate equation is expressed as follows:

$$dq_t/d_t = K_2 (Q_e - Q_t)^2$$
 (11)

where, K_2 (mg/min) is The rate constant of pseudo second order adsorption. From the boundary conditions t = 0 to t = t and $Q_t = 0$ to $Q_t = Q_t$, the integrated form of equation:

$$d/d_t qt = K_2 (q_e - q_t)^2$$
 (12)

This is the integrated rate law for a pseudo second order reaction. This can be writing in linear form as shown below:

$$1/q_e - q_t = 1/q_e + K_{2t}$$
(13)

This can be writing in a linear form as follows:

$$t/q_t = 1/K_2 q_e^2 + 1/q_t$$

From the equation above, graph of t/q_t is plot against t, where qe and K_2 is slope and intercept respectively (Demirbas, 2007).

Adsorption thermodynamics: Thermodynamic parameters were determined using the relation below. These parameters are; Change in the Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°):

 $\Delta G^{0} = -RTlnKc$ $lnK_{C} = \Delta S^{0}/R - \Delta H^{0}/RT$

where,

R = The universal gas constant (8.314J/mol.K), d at T (k), respectively. Kc can be calculated from the relation below:

 $K_c = C_{ad}/C$

RESULTS

From Fig. 1, the adsorption of Mn (II), Ni (II) and Cd (II) ions were found to be pH dependent. The rate of adsorption increased with increase in pH. Cd (II) ion was adsorbed more at every pH than both Mn (II) and Ni (II) ions. Mn (II) ion had highest adsorption at pH 7; Cd (II) and Ni (II) ion were at pH of 6 respectively.

From Fig. 2, the adsorption process was time dependent in the sense that as the contact time increases the adsorption of Ni (II), Mn (II) and Cd (II) onto the surface of the adsorbent also increases until the equilibrium was attained at 60 min.

It was deduced from the above table that as the metal ion concentration increases, the amount of metal



Fig. 1: The effect of pH on the adsorption of Mn (II), Ni (II) and Cd (II) ions



Fig. 2: The effect contact time on the adsorption of Ni (II), Mn (II) and Cd (II)

ion adsorbed also increased. Comparing the three metal ions it was also observed that at each variation, Cd (II) ion had highest adsorption followed by Ni (II) and finally by Cd (II) ion. The trend of adsorption was (Mn<Ni<Cd).

DISCUSSION

Effect of pH on biosorption of metal ion concentration: pH is an essential factor to be considered in the process of adsorption of metal ion from aqueous solution in the sense that its account for the protonation of metal binding sites (Demiral et al., 2008). The uptake of Ni (II), Cd (II) and Mn (II) by cow horn was a function of pH as shown in Fig. 1. At low pH 1-2, Ni (II), Mn (II) and Cd (II) removal was minimal; this was probably as a result of competition between the metal ions and the hydrogen ion on the sorption site with obvious dominance of hydrogen ion which resist the advance of metal cation as a result of abhorrent or repulsive force. As the pH increased between 3 and 4, the hydronium ion was getting deprotonated and more metal ion was removed. The maximum uptake was observed when the pH increased to 6 for Ni (II) and Cd (II) ion while Mn (II) ion was at pH of 7. Similar results were also reported in literature on Hazelnut shell by Demirbas (2007), Gallus domesticus by Kalyani et al. (2009) and goat hooves by Egila et al. (2012). The consequential effect of pH could also be explained using the mechanism of the ion-exchange in which the important role was played by the thiol (SH) group present in the keratinous substrate. As the pH increase between 5-6, the thiol group (SH) was exposed which increase the negatively density charge on the surface of the adsorbent and therefore increasing the attraction and the desirability of the metallic ions with a positive charge on the adsorbent and give a greater chance to adhere on the adsorbent surface. Thus, as the pH increases, the binding sites starts deprotonating and making it more available for more uptake of the metal ion, this continues until pH of 7 for Mn (II) ion. At pH higher than 6 for both Ni (II) and Cd (II) the adsorption decreases as a result of decease in the protonation of the functional group of the adsorbent, the same trend was observed for Mn (II) ion at pH 8. This corroborated the earlier studies by Esposito et al. (2002).

Effect of contact time: The effect of contact time on the adsorption of Ni (II), Mn (II) and Cd (II) is shown in Fig. 2. It was observed that as the agitation time increased the percentage of metal ion adsorbed also increased from 20 to 60 min when the equilibrium was attained. Further increase in agitation time resulted into decrease in amount of metal ions sorbed. The maximum percentage of Ni (II) ion removed was 75%, 57% for Mn (II) ion and 94% for Cd (II) ion. It was observed that more of Cd (II) ion was removed than Mn (II) and Ni (II) ion. This observed differences could arise as a result of Cd (II) ion having greater ionic radii of (0.95A) than Ni(II) (0.69A) and Mn (II) (0.67A°). The trend of adsorption was Cd (II) >Ni (II) >Mn (II) ion. This pattern of adsorption conforms with what was obtained by Ekop and Eddy (2009) while investigating the adsorptive ability of Helix aspera shell.

The effect of the initial metal ion concentration: The effect of variation of initial metal ion concentration on the adsorption is shown in Fig. 3. The results revealed that as the concentration of the metal ions increases the amount adsorbed by the adsorbent also increases. The plausible reason could be based on the progressive increase in the columbic interaction or electrostatic effect between the cationic species in the solution and the active sites of the adsorbent. Also as the metal ion concentration increases, more of the adsorptive sites are covered. Therefore, at higher initial metal ion stowards the



Fig. 3: Effect of variation of initial metal ion concentration on adsorption of Ni (II), Mn (II) and Cd (II) ions

Table 1: Langmuir isotherm parameters for the bio-sorption of Mn (II), Ni (II) and Cd (II) ion by cow horn

Metalion	Q _{max} mg/g	$K_L (mg/L)$	\mathbb{R}^2	RL
Mn (II)	9.62	0.0110	0.984	0.097
Ni (II)	35.71	0.0018	0.989	0.098
Cd (II)	62.50	0.0015	0.992	0.099

Table 2: Temkin isotherm parameters for the bio-sorption of Mn (II), Ni (II) and Cd (II) ion by cow horn

Metalion	a	b	\mathbb{R}^2	R _L
Mn (II)	0.908	-1.294	0.872	0.090
Ni (ÎI)	1.358	-2.732	0.945	0.096
Cd (II)	1.554	-3.284	0.977	0.099

active sites also increases. This could also be attributed to the fact that the adsorbent is composed of porous structure with large internal surface area. This observation was similar to what was reported on the adsorption of methylene blue onto peanut hull by Gong *et al.* (2005).

Adsorption isotherm: The results of the isotherm parameters were shown in Table 1 and 2. The results as shown in the Tables were obtained from the plots as shown in Fig. 4 to 9. From the two table, Langmuir constant has highest adsorption capacity ($q_{max} = 62.50$ mg/g) for Cd (II) compared to that of Mn (II) and Ni (II) ions ($q_{max} = 9.62$ and 35.71 mg/g) respectively. The correlation coefficients R², value for Mn (II), Ni (II) and Cd (II) were 0.984, 0.989 and 0.992 respectively. The R_L value for the Langmuir isotherm for manganese, nickel and cadmium are 0.098, 0.098 and 0.099 respectively. On the contrast, the correlation coefficient for Temkin isotherm for Mn (II), Ni (II) and Cd (II) ions were 0.872, 0.945 and 0.977 respectively. The equilibrium binding constant for the three metals were 0.908, 1.385 and 1.554 respectively, the R_L value for Mn (II), Ni (II) and Cd (II) are 0.090, 0.099 and 0.099 respectively. By comparing the values of the correlation coefficients of the two isotherms, it shows that the Langmuir model better represents the biosorption process than Temkin model. Similar result



Fig. 4: Langmuir adsorption isotherm plot of Mn (II) ion



Fig. 5: Langmuir adsorption isotherm of Cd (II) ion



Fig. 6: Langmuir adsorption isotherm of Ni (II) ion



Fig. 7: Temkin adsorption isotherm plot for Mn (II)



Fig. 8: Temkin adsorption isotherm plot for Ni (II) ion



Fig. 9: Temkin adsorption isotherm plot for Cd (II) ion

was obtained by Stevens and Nnabuk (2008). Also, the higher correlation coefficient R^2 for Cd (II) ion revealed that the adsorbent has greater affinity for its removal than Ni (II) and Mn (II) ion. This observation might be attributed to the large ionic radii (0.95 A^0) of Cd (II) ions as compared to Mn (II) ion (0.67 A^0) and Ni (II) with (0.69 A^0). Another plausible reason for this occurrence in adsorption could be explained in term of the size of hydrated cadmium ion which becomes smaller in solution when compared with that of Mn (II) and Ni (II) ion as such and the uptake mechanism of the metal ions was affected by stearic hinderance (Vijayaraghavan *et al.*, 2006).

Effect of temperature: The thermodynamic parameters determined from the biosorption of Mn (II), Ni (II) and, Cd (II) onto cow horn, which includes; standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) are shown in Table 3. The positive and larger values of ΔG° indicated that the process is feasible but nonspontaneous. The positive values of ΔH^0 for the adsorption of the three metal ions implied the biosorption processes was endothermic in nature and this could also be supported with rise in temperature

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(II) and Cd (II) on cow horn				
Metalion	ΔH° (Kj/n	nol) $\Delta S^{\circ} (J/mc$	ol/K) $\Delta G^{\circ}(Kj/K)$	R^2
Mn (II)	1028	-2.31	1,733.90	0.765
Ni (II)	637.9	-1.45	1,080.15	0.556
Cd (II)	220.5	-0.50	382.87	0.736

Table 3: Thermodynamic parameters for the biosorption of Mn (II), Ni



Fig. 10: Pseudo-first order plot for the adsorption of Mn ion





Fig. 12: Pseudo-first order plot for Cd (II) ion

That equally results into increase adsorption capacity. The positive value of ΔH^0 also implies the presence of energy barrier in the adsorption process



Fig. 13: The pseudo-second-order kinetic plot for the adsorption of Mn (II) ion



Fig. 14: The pseudo-second-order kinetic plot for the adsorption of Ni (II) ion



Fig. 15: The pseudo-second-order kinetic plot for the adsorption of Cd (II) ion

(Babarinde *et al.*, 2012). The negative values of ΔS° imply a decrease in the randomness at the solid/solution interface of the adsorbent during the adsorption of Cd (II), Ni (II) and, Mn (II) ions unto adsorbent surface. This is in collaboration with what

Table 4: Parameters for the pseudo-second order kinetics plot for the bio-sorption of Mn (II). Ni (II) and Cd (II) ion by cow horn

010-501		and Cu (II) Ion by	
Metal ion	K ₂ g/gm/min	q _e mg∕g	R ²
Mn (II)	8×10 ⁻¹	4.977	0.555
Ni (II)	0	5.575	0.641
Cd (II)	8.8×10^{-1}	5.528	0.946

Table 5: Parameters for the pseudo-second order kinetics plot for the bio-sorption of Mn (II), Ni (II) and Cd (II) by cow horn

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Metal ion	K ₂ g/mg/min	q _e mg/g	\mathbb{R}^2
Mn (II)	4.9×10 ⁻²	4.977	0.555
Ni (II)	3.0×10 ⁻¹	5.575	0.641
Cd (II)	2.8×10 ⁻¹	5.582	0.946

has been reported in the literature by Torab *et al.* (2010).

As the temperature increases, the adsorption capacity of the adsorbent also increased. This implies that, the adsorption process was chemisorption in which higher activation energy is needed. This may possibly due to the increase in diffusion of the metal ion into the pores of the adsorbent surface and the development of new binding sites at higher temperature (Babarinde and Babalola, 2010).

Kinetic study: The comparism of this kinetic models based on the linear regression correlation coefficient (\mathbb{R}^2) for both pseudo-second and pseudo-first order kinetic indicated that pseudo-second order best described the biosorption process as shown in Fig. 10 to 15 and Table 4 to 5. This data also predicted that the efficiency, fittingness and applicability of pseudo-second order kinetics was more than pseudo-first order kinetics model. The higher value of kinetic constant also favor pseudo-second order and this suggest that chemisorption type of interaction was developed between the aqueous solution and the adsorbent. This result is in conformation with what had been earlier reported in the literature by Ejikemi *et al.* (2011) and Ncibi *et al.* (2009).

CONCLUSION

From the obtained results in this study, it could therefore be concluded that, the adsorbent produce from cow horn has a strong attraction for the removal of Cd (II) ion from aqueous solution more than Ni (II) and Mn (II) ions respectively. The equilibrium data was best fitted to Langmuir adsorption isotherm which indicates that the adsorption of Mn (II), Ni (II) and Cd (II) ion was homogenous and monolayer. The thermodynamic investigation shown that the process was feasible and endothermic but not spontaneous and finally pseudosecond order model was use to describe the binding of Mn (II), Ni (II) and Cd (II) ion respectively to the adsorbent.

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