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Heavy Metals Removal from Polluted Water by Activated Carbon Prepared from Pomegranate Peel

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Abstract: Pomegranate peel (PP) and activated carbon produced from Pomegranate peel (PPAC) was used as adsorbent to remove Pb^{2+}, Cu^{2+} and Cr^{2+} ions from polluted water. The activated carbon produced was chemically activated with zinc chloride. Batch adsorption experiment was conducted to examine the effects of contact time, pH and initial concentration of Pb^{2+}, Cu^{2+} and Cr^{2+} from the wastewater. The effects of initial concentration (10-100 mg.L^{-1}), contact time (5-240 min) and pH (2-10) have been studied at room temperature. The removal increased as the initial concentrations decreased. A maximum removal observed at an adsorbent dosage of 1.5 gm for an initial concentration of 10 mg.L^{-1} at pH (6), metal uptake increased with time. After that has the comparison of bisorption of heavy metals by (PP) with bisorption of (PPAC), the results showed that activated carbon produced from pomegranate peel (PPAC) is a better biosorbent from pomegranate peel (PP), the percentage removal reached almost 98% for Pb^{2+}, 92% for Cu^{2+} and 75% for Cr^{2+} in the case of (PPAC). While the percentage removal reached almost 88 % for Pb^{2+}, 66 % for Cu^{2+} and 54 % for Cr^{2+} in the case of (PP).

Key words: Biosorotion・Heavy metals・Wastewater・Polluted water

INTRODUCTION

The contamination of water by toxic heavy metals through the discharge of industrial wastewater is worldwide environmental problem. The environmental impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscape and water bodies [1]. Authorities enforcing these standards further require the treatment procedure to be environment friendly [2]. Heavy metal pollution in the aquatic system has become a serious threat today and has great environmental cancer, as they are non-biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water. The metal increase in concentration at every level of food chain and are passed onto the next higher level a phenomenon called bio magnification [3]. Different methods used for the removal of metals are filtration, chemical precipitation, coagulation, solvent extraction, electro dialysis, ion-exchange, membrane process and adsorption [4]. Ion-exchange and adsorption are the most common and effective processes for this purpose. The major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment becomes costly affair and is not eco-friendly. Therefore removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance [5, 6]. In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain wastes from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources which are widely available and are environmentally friendly. Some previous investigations on the removal of heavy metal ions with many agricultural byproducts have been reported [7].

Activated carbon and different types of ion-exchange resins are very often used. However, their high price and regeneration cost have encouraged research work to find low-cost adsorbing materials for the removal of heavy metals. Several materials in this category have been successfully used for the removal of heavy metal ions from industrial wastewater [8-14].Copper is generally considered to be toxic to man at concentration exceeding 5mg/L, imparts color and undesirable taste. The World

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health Organization's guide line for drinking water based on its staining properties is 1mg/L [15]. Beyond the permissible level, copper causes acute and chronic disorders in human beings such as gastrointestinal catarrh, cramps in the calves, hemochromatosis and skin dermatitis brass chills usually accompanied by high fever [16, 17]. Industries discharging copper in the wastewater are electroplating industries, pulp and paper mills, fertilizer plants, steel work foundries, petroleum refineries, aircraft and finishing, motor vehicles and non-ferrous metalwork [18-20]. Pomegranate peel, a by-product of the pomegranate juice industry is an inexpensive material. It is composed of several constituents, including polyphenols, ellagic tannin and Gallic and ellagic acids [21-24]. Pomegranate belongs to the genus *Punica*, order Myrtales and family *lythraceae*, which is a tropical family species with 73 genera and 850 species. The genus *Punica* contains several that bear edible fruit. Most of the fruit trees that are commonly known as pomegranate belong to the species *P. granatum*. The other edible *Lythraceae* species generally have lower quality fruit and are commonly referred to as wild pomegranate [22].

In this study, the locally available pomegranate biomass and activated carbon preparing from pomegranate were used to study the adsorption performance from single metal ion aqueous solution. The effects of solution contact time, pH and adsorbent concentration, on Pb(II), Cu(II) and Cr(II) were investigated in detail.

MATERIALS AND METHODS

Experimental Procedure

Biosorbent Preparation: Pomegranate peel was used as a biosorbent for the removal of heavy metals. Pomegranate peel was washed several times with double distilled water, till the water was clear of all coloration and finally dried in an air oven at 60°C for 24 hrs. After drying the adsorbent was sieved, it was labeled by (PP). 250 g of the smaller pieces was soaked for twenty four hours in a solution prepared from phosphoric acid and zinc chloride in ratio of 1:1, then dried and carbonized, it was labeled by (PPAC).

The yield prepared biosorbent was calculated from the following equation [25]:

$$\% yield = \frac{W_o - W_e}{W_o} \times 100 \quad (1)$$

where W_O is the mass of material before carbonization, W_C is the mass of material after carbonization. The physico-chemical characterization of adsorbents were measured using standard procedures. The data are illustrated in Table 1.

FTIR spectra of the adsorbents (PP and PPAC) were taken with a Fourier-transform infrared spectrophotometer (JASCO FT/IR-410, Japan).Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra tests.

Adsorption Studies: Adsorption studies were carried out by batch process. 1.5 g adsorbent was placed in a conical flask (250 ml), 25 mL solution of metal ions of desired concentration was added and the mixture was shaken in rotary shaker at agitation rate of 200 rpm and in an isothermal (25°C) for four hours. The mixture was then filtered by what man filter paper No. 41 and final concentration of metal ions was determined in the filtrate by atomic absorption spectrometry (AAS) (Model Z-8100 polarized Zeeman). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration. The removal (R) efficiency of each metal was calculated according to the following equation [26]:

$$\% R = \frac{C_o = C_f}{C_o} \times 100 \quad (2)$$

where C_o and C_f (mg /l) are the initial and final concentration of each element present in wastewater before and after adsorption.

Effect of pH: The effect of pH on the adsorption of Cu(II), Cr(II) and Pb(II) were studied as follows. The pH of the solutions was adjusted and controlled in the range of 2 - 10.

100 mL of metal selected was taken in a beaker. The pH of solution was adjusted by adding 0.1N HCl or 0.1N NaOH solution. The concentration of metal selected in this solution was 100 mg/l. 25 mL of this solution was taken in conical flask and treated with 1.5 g adsorbent. The mixture was filtered and final concentration of metal selected in filtrate was determined as described above.

Effect of Time: A series of 250 mL conical flasks, each having 1.5 g adsorbent and 25 mL solution of known metal concentration were shaken in a shaker incubator and at the predetermined intervals, the solution of the specified flask was taken out and filtered.

The concentration of metal in the filtrate was determined by AAS and the amount of metal adsorbed in each case was determined as described above.

Table 1: The physical properties of the different types of the adsorbents

Adsorbent type	Micro pore diameter (cm^3/g)	Average pore diameter (cm^3/g)	Bulk density (kg/m^3)	Micro pore area (m^2/g)	Moisture content (%w t)	Ash content (% w t)	Yield (%)
PP	0.063	0.24	84.3	10.55	19.32	12.75	--
PPAC	0.18	0.32	75.1	133.5	3.11	5.98	48

Samples were collected at definite time intervals viz. 5, 10, 15, 20, 30, 60, 120, 180 and 240 min to analyze the residual metals concentration.

RESULTS AND DISCUSSION

Characteristics of Adsorbing Material: A scanning electron microscope (SEM) was used to examine the surface of the two adsorbents and SEM photographs. Fig. 1 shows progressive changes in the surface of particles. Table 1 shows the physical characteristics of the two adsorbents used in the present study.

The FTIR spectra of PP, PPAC and PP after biosorption process (PPAB) and PPAC after biosorption process (ACAB) were carried out as a qualitative analysis to determine the main functional groups present in the adsorbent. Table 2 and Fig. 2 show the tabulated data for FTIR spectra band assignments for PP, PPAC, PPAB and ACAB samples. These spectra described the various changes that occurred in the PP, PPAC, PPAB and ACAB samples. The spectra for PP showed long bandwidth 3730-3298 cm^{-1} which indicates the O-H stretching of hydroxyl group. The C=C stretching of alkyne group was detected at bandwidth 2826-2862 cm^{-1}. The C-N stretching of aliphatic primary amine group was detected at bandwidth 1229 cm^{-1}. The C=O stretching of lactones, ketones and carboxylic anhydrides functional groups were detected at bandwidths of 1820-1880 cm^{-1}. Some of the peaks disappears or shifts in the PPAC due to heating at high temperature. Similar results were obtained in the study of the effects of acid leaching on porosity and surface functional groups [27]. Some of the peaks disappears or shifts in the PPAB and ACAB (Table 2). The C-H stretching in alkanes or alkyle group 1361 cm^{-1}, C-N stretching of aliphatic primary amine group (1029 cm^{-1}) and C-O (1226 cm^{-1}) disappear in PPAB and ACAB due to complex formation. Complex formation occurred between N or O atoms and metal ions because Cu, Pb and Cr are all transition metals which have empty orbital that can be occupied by extra electrons of N or O in PP and PPAC.

Effect of Initial Element Concentration: The adsorption of Pb^{2+}, $Cu^{2+}$and Cr^{2+} onto pomegranate peel at different initial concentrations from 10 to 100 mg l^{-1} were studied and the results were represented by Fig. 3. The percentage removal reached almost 88 % for Pb^{2+}, 66 % for Cu^{2+} and 55 % for Cr^{2+} ions at lower initial concentrations of metals. It was shown that the percentage of elements removal decreased as the initial concentrations of elements increased which clearly indicate that the adsorption of elements from its aqueous solution was dependent on its initial concentration. This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above certain concentration. Increase of the initial metal concentration results in a decrease in the initial rate of external diffusion and increase in the intra-particle [28]. In the process of Pb^{2+}, $Cu^{2+}$and Cr^{2+} adsorption, first metal ions have to encounter the boundary layer effect and then diffuse from boundary layer film onto pomegranate peel biomass and finally, it has to diffuse into the porous structure of it. These phenomena will take relatively longer contact time. Among the three metals, the biomass exhibited the lowest adsorption efficiency for Cr^{+2} from 55 to 38% for lower and higher concentration. The removal efficiencies for the other two metals were in a similar range of about 66-88% at concentration (10 mg/l) and from 50-65 % at concentration (100 mg/l). After that has the comparison of bisorption of heavy metals by normal pomegranate peel (PP) with bisorption of heavy metals by activated carbon prepared from pomegranate peel (PPAC) and the results were represented by Fig 4. The percentage removal reached almost 98% for Pb^{2+}, 92% for Cu^{2+} and 75% for Cr^{2+} ions at lower initial concentration, 83% for Pb^{2+}, 80% for Cu^{2+} and 68% for Cr $^{2+}$ions at higher initial concentration of metals. It was shown that the percentage elements removal increased in biosorption by activated carbon.

Effect of pH: The pH of the wastewater is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 10 under the precise conditions (At optimum contact time of 60 min, 150 rpm shaking speed, with 1.5 gm of the adsorbents used and at a room temperature of 32°C). From Figure 5, with pomegranate peel and Figure 6, with activated carbon from pomegranate peel used as adsorbent, it was observed that with increase in the pH

Table 2: Comparison of infrared bands in 4000-400 cm^{-1} spectra

	Wavenumber/cm^{-1}			
Functional group of adsorbent	PP	PPAC	PPAB	ACAB
O-H stretching of hydroxyl group	3220-3498	3280-3510	3230-3490	3212-3460
C=C stretching of alkyne group	2826-2862	2858-2940	2840-2855	2860-2820
C=O stretching of lactones, ketones	1820-1880	1740-1790	1760-1794	1755-1761
C-O stretching vibration in quinine structure	1226	-	-	-
C=C of aromatic ring	-	2460	2495	-
C-H stretching in alkanes or alkyle group	1361	-	1350	-
C-N stretching of aliphatic primary amine group	1029	-	-	-

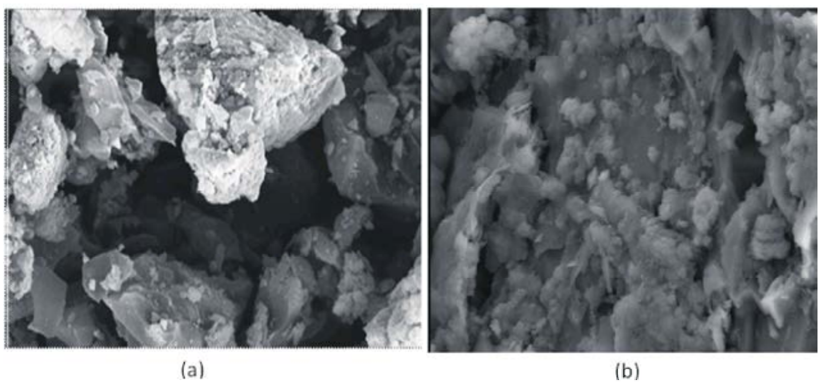

Fig. 1: Scanning electron micrographs for the two adsorbents, (a) pomegranate peel (PP) and (b) activated carbon from pomegranate peel (PPAC)

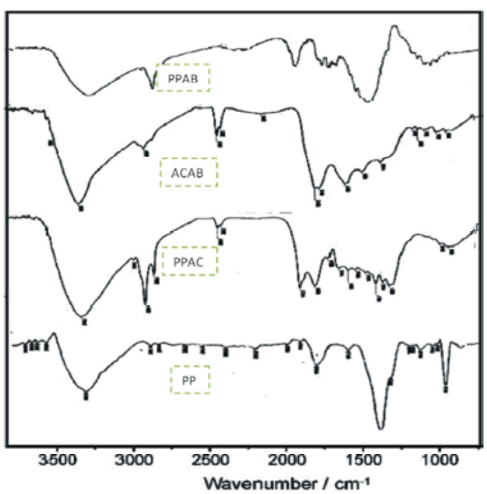

Fig. 2: FTIR spectra; PP, PPAC, ACAB and PPAB from bottom to top, respectively

(2-6) of the wastewater, the percentage removal of metal ions (Pb, Cu and Cr) all increased up to the pH 6. At pH 6, maximum removal were obtained for all the three metal ions, with 88% removal of Pb (II), 67% of Cu(II) and 54% removal of Cr(II) with pomegranate. While 98% removal of Pb (II) ion, 92% of Cu(II) and 75% removal of Cr(II) with activated carbon. The other important reason is that at lower pH values, the cell wall ligands would be closely associated with the hydronium ions (H_3O^+) that restrict access to legends by metallic ions as a result of repulsive forces. This repulsion is stronger at lower pH. On increasing pH more ligands (Carrying negative charges) would be exposed with the subsequent attraction of positively charged metal ions. Similar results were reported by previous investigators. Some researchers stated that the increase in metal biosorption after pre-treating the biomass, could be due to the removal of surface impurities and exposure of latent binding sites for metal biosorption [29].

Effect of Contact Time: The relation between adsorption of Pb^{2+}, $Cu^{2+}$and Cr^{2+} and contact time was investigated to identify their removal rate. Figure 7, with pomegranate and Figure 8, with activated carbon from pomegranate, show the percentage removal of each element at initial concentration (25 mg /l) and pH was adjusted at 6.0. It was found that, more than 50 % removal of Pb, 30 % removal of Cu and 20 % Cr in the first 5 min in pomegranate cortex and more than 60 % removal of Pb, 55 % removal of Cu and 45 % Cr in the first 5 min in activated carbon. After 60 min, more than 80 % removal of Pb, 60 % removal of Cu and 45 % Cr in pomegranate cortex and more than 90 %

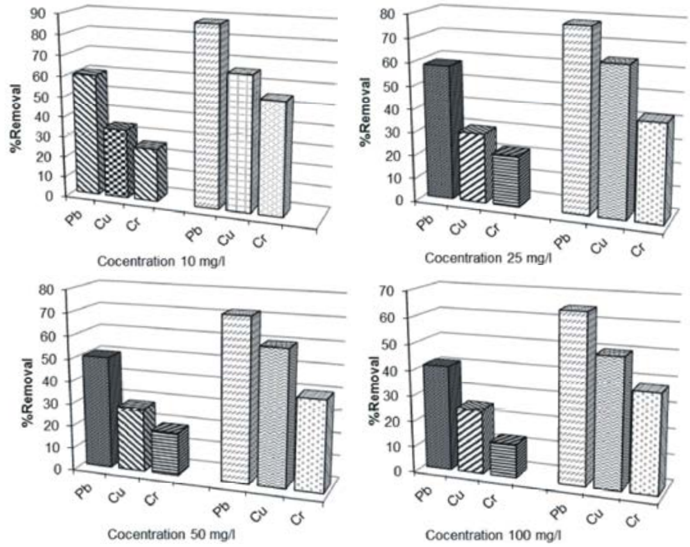

Fig. 3: Relation between removal percent of elements and their different initial concentrations onto pomegranate peel. The black bars indicate one load and the gray bars indicate reloaded twice

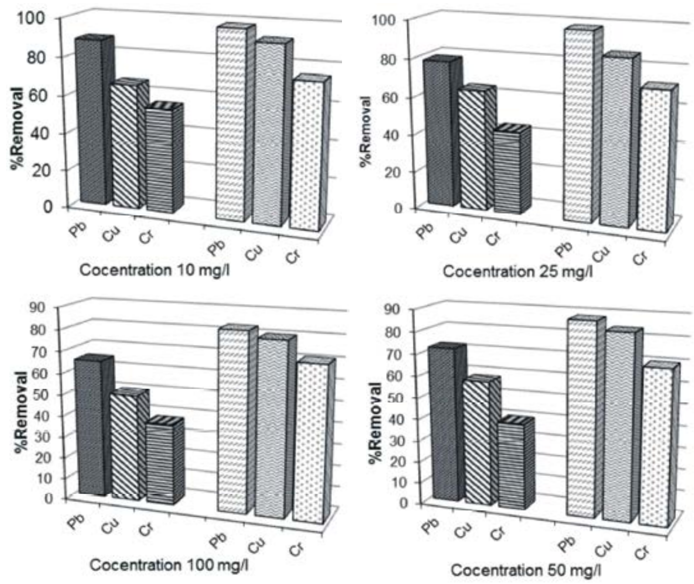

Fig. 4: Relation between removal percent of elements and their different initial concentrations. The black bars indicate removal by normal pomegranate peel (PP) and the gray bars indicate removal by activated carbon prepared from pomegranate peel (PPAC)

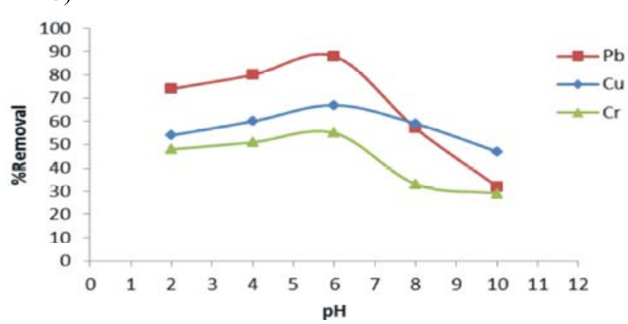

Fig. 5: Effect of pH on Pb(II), Cu(II) and Cr (II) uptake using pomegranate waste biomass

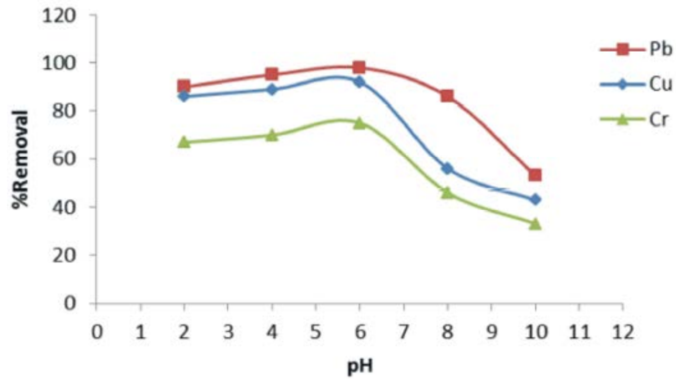

Fig. 6: Effect of pH on Pb(II), Cu(II) and Cr(II) uptake using activated carbon from pomegranate peel

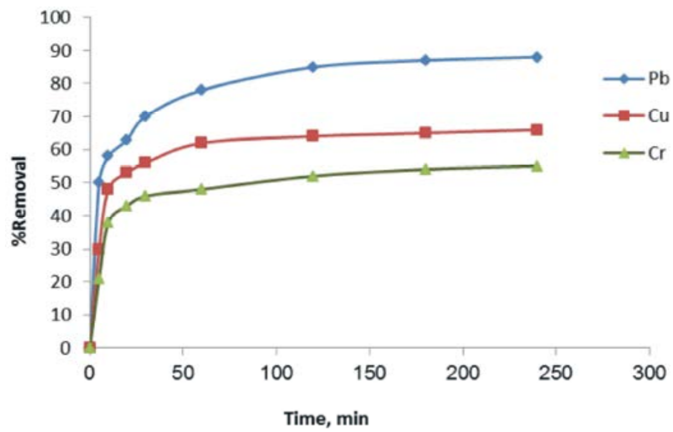

Fig. 7: Effect of contact time on the removal of different initial concentrations of Pb^{2+}, Cu^{2+} and Cr^{2+} using pomegranate waste biomass

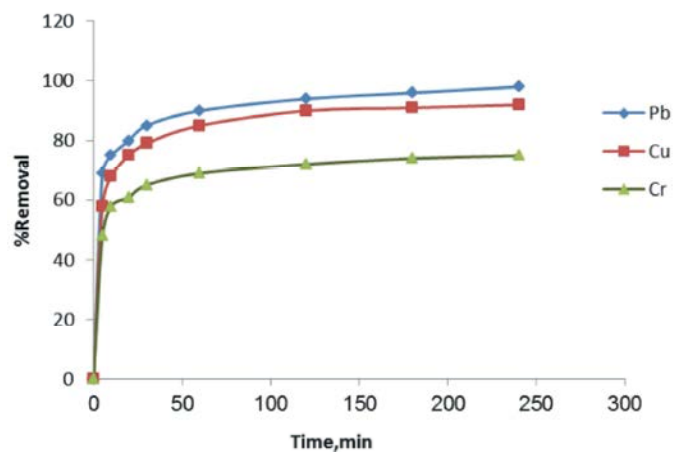

Fig. 8: Effect of contact time on the removal of different initial concentrations of Pb^{2+}, Cu^{2+} and Cr^{2+} using activated carbon from pomegranate peel

removal of Pb, 85 % removal of Cu and 70 % Cr in activated carbon. The removal percentage values of elements by pomegranate and activated carbon from pomegranate biomass were found to be in the order of $Pb^{2+} > Cu^{2+} > Cr^{2+}$. Therefore, it can be concluded that the rate of element binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period. The slow rate of element adsorption after the first 60 min is probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent [30].

CONCLUSIONS

Pomegranate waste biomass (PP) is a useless material without any commercial importance. Obtained results clearly demonstrated that pomegranate waste biomass can be effectively used for Pb^{2+}, Cu^{2+} and Cr^{2+} removal from wastewater. Activated carbon produced from pomegranate peel (PPAC) is a good adsorbent removal of lead, copper and chromium ions. The results showed that activated carbon produced from pomegranate (PPAC) is a better biosorbent from pomegranate peel (PP). Optimized pH, initial concentration and contact time for Pb^{2+}, Cu^{2+} and Cr^{2+} uptake by pomegranate waste biomass and activated carbon produced from pomegranate were 6, 10 mg/L and 60 min.

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