

Effect of humic acid on transformation of soil heavy metals

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Abstract. The pattern of transformation among different fractions of heavy metals in soil draws great attention. This article investigated the effect of humic acid on soil heavy metal under different pH and temperature. The results showed that with the increasing of the concentration of humic acid, the concentration of available Cu, Pb decreased greatly, though the decrease of available Cd was light. Also, pH of soil had certain impact on the concentration of available Cu, Pb, Cd while the influence of environmental temperature was minor. The removal efficiency of contaminated soil was 57.283% (Cu), 2.645% (Cd) and 15.485% (Pb) while it could reach more than 98% in contaminated solution.

1. Introduction

At present, China is paying close attention to the heavy metal contaminated soil [1]. The heavy metal pollution of soil is persistent and difficult to transform, which affects the soil fertility and biochemical activity, and enters the food chain through plant's absorption, causing an adverse impact on people's health. The existence of heavy metals in the soil can be divided into six forms: water-soluble, active, carbonate, organic, iron-manganese, and silicic acid. Among them, the water-soluble and active state are the effective modes of plant, which are easy to be absorbed by plants, while the rest are not [2]. A sequence of factors like soil pH, oxidation-reduction potential, cation exchange capacity, soluble organic matter and so on will affect the solubility and mobility of heavy metals in the soil [2,3]. Udom [4] found that the complexation of organic matter and heavy metals can significantly reduce the migration and bioavailability of pollutants in the soil. Zhang Yali [5] also pointed out that organic fertilizers have the effect of reducing the bioavailability of heavy metals in soil and changing the morphology of Cd.

Humic acids (HAs) have a unique structure and are widely distributed in the soil system. The application of HAs to heavy metal remediation in the soil has been extensively studied. Bruna Alice Gomes De Melo et al. [6] found that the cationic metal interacts with the phenolic and carboxyl groups on the molecular chain of HAs to form spherical compounds, which claimed the soil remediation mechanism of HAs. Applying HAs to the soil can reduce the content of soluble heavy metals and the content of the organic form of Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} , so as to the activity, toxicity and bioactivity of Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} in the soil [7]. Yates & von Wandruszka's [8] experiments also showed that HAs had the greatest affinity with Pb^{2+} , Cu^{2+} .

However, when the external environment changes, there is less concern about the effect of HAs applied to heavy metals contaminated soil. In this study, we applied different contents of HAs to the



soil that was in various conditions (pH and temperature) contaminated by Cu, Pb and Cd, in order to explore the effect and law adsorbed by HAs, which has great practical significance.

2. Materials and methods

2.1. Experimental material and instrument

The experimental sample was collected from 10-20cm surface soil layer of uncontaminated plant-covered area in Zhongnan University of Economics and Law. Remove the impurities and pack with polyethylene bag. Air and mix the sample after filtrating by 10-mesh sifter. Immersed 3kg sample with 1L liquor (30mg/L cadmium nitrate, 1500mg/L cupric nitrate, 3000mg/L lead nitrate). Settle the sample for 30 days and filtrate with 100-mesh sifter.

The sample was preprocessed by the Jena Top Wave microwave digestion instrument. The heavy metal was measured by Jena Znieet 700P atomic absorption spectrophotometer.

2.2. Experimental approach

The effects of exchangeable heavy metal were measured in different percentage of humic acid dosage (0.2%, 0.5%, 1%, 3%, 5%), temperature (10°C, 20°C, 30°C, 40°C, 50°C) and pH (3, 5, 7, 9, 11). The measurement referred to Tessier's five-step approach.

Put 2.50g experimental sample in 50ml centrifuge tube. Add 10ml distilled water and humic acid into the centrifuge tube. Adjust the pH by 0.1mol/L NaOH. Shake the centrifuge tube for 18 hours at the setting temperature. Took down the tube after shaking and added 10ml MgCl₂ (pH=7,2mol/L) in it. Shake the tube for another hour. Save the sample after filtrating it by 0.22μm filter membrane.

Take 0.125g humic acid and 20ml simulative solution (cupric nitrate 12mg/L, lead nitrate 68mg/L, cadmium nitrate 0.76ml/L) in tube. Shake it at 20°C for 18h. Filtrate with 0.22μm filter membrane.

3. Results and discussion

3.1. Leaching pattern in man-made contaminated soil

As for man-made contaminated soil, fractions of heavy metal in soil transform when time elapsing, thus making it important to study leaching pattern in man-made contaminated soil. Fig.1 shows that pH and temperature both have an obvious impact on available state of heavy metals. For available Pb and Cu, their concentrations declined while temperature declined or pH rose. The influence of temperature is mild within the range 20°C~40°C, and there is a sharp drop when pH gets 11; for available Cd, the leaching amount is comparatively low when the pH ranging 3~11 and will increase slightly in strong alkaline environment. Also, there's great difference in leaching amount under different temperatures.

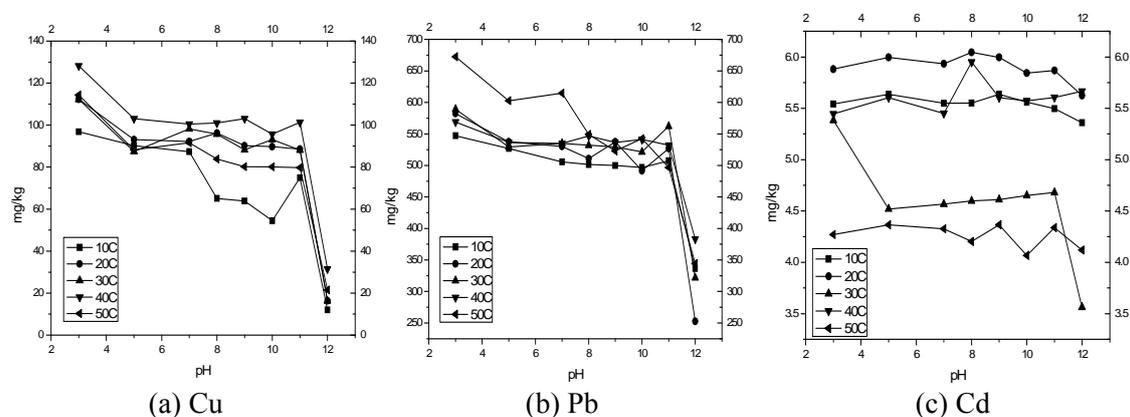


Figure 1. Concentration tendency of available Cu, Pb, Cd in man-made contaminated soil

3.2. The impact of humic acid on different heavy metals

3.2.1. The impact of humic acid on Cu. The ratio of humic acid, pH, temperature all have an obvious impact on the concentration of available Cu in soil. As is seen from fig.2, the concentration of available Cu in soil declined sharply when the ratio of humic acid or pH rose, while temperature showed little influence on it under alkaline environment. The declining trend is comparatively smooth when the ratio of humic acid varied between 0 and 1.00%, however, it become somewhat steep after continuing increasing.

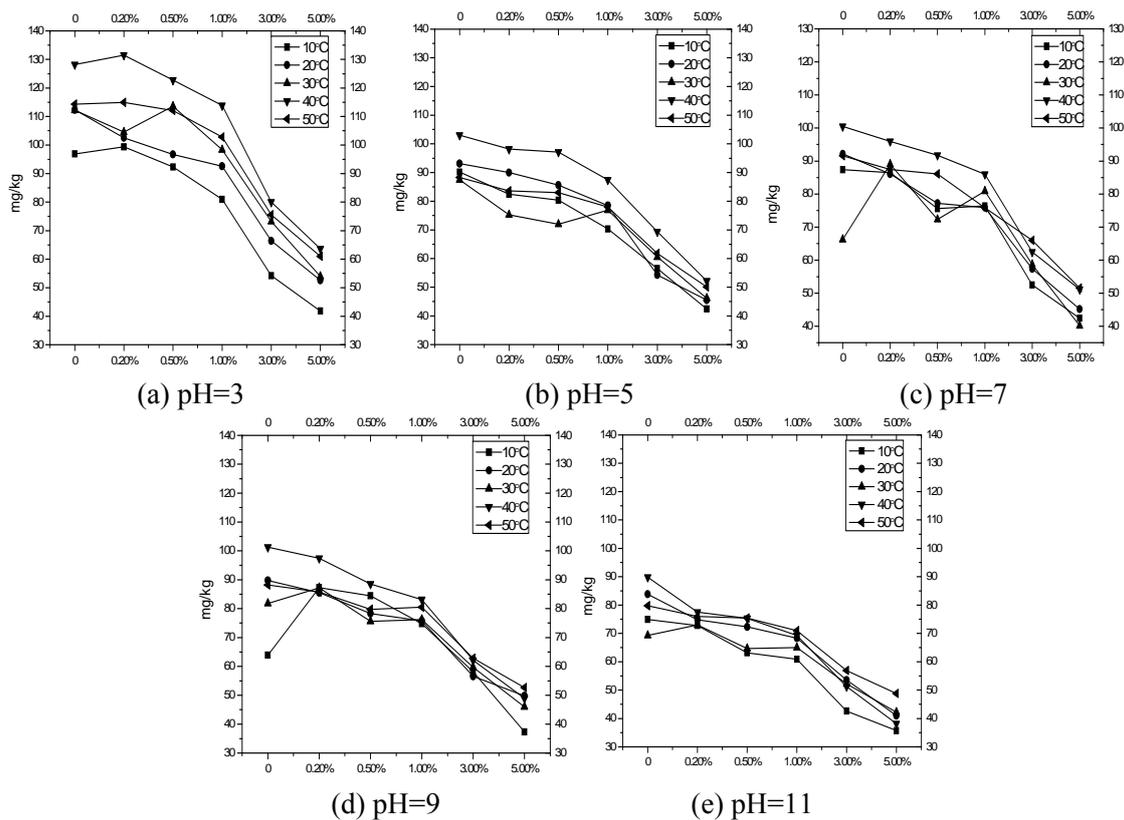


Figure 2. Concentration tendency of available Cu

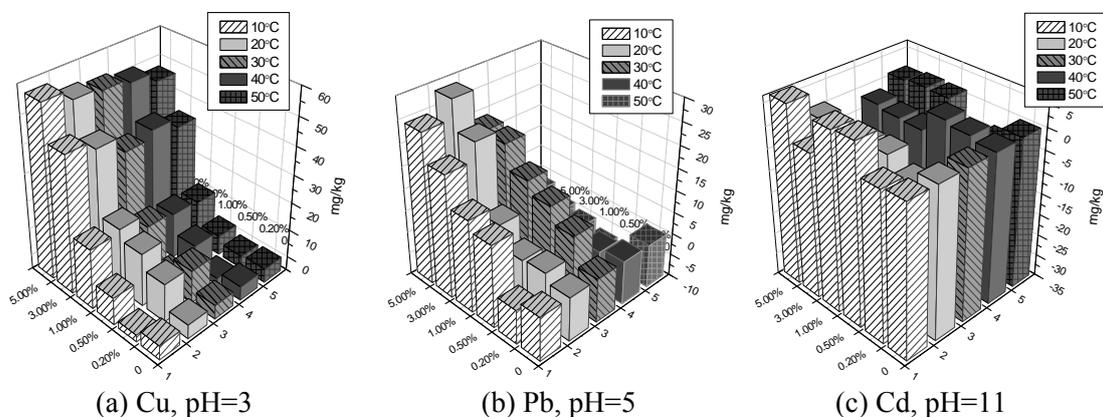


Figure 3. The influence of humic acid on available

The ratio of humic acid and temperature both have an obvious impact on the removal of available Cu in soil. Fig.3(a) shows that the removal efficiency was around 0~55% basically. This rose with more humic acid added, though it won't be much affected by pH. Under acidic environment, its negative correlation with temperature was obvious, and the removal efficiency worsened under 30°C with the increasing of pH.

From fig.2 and fig.3(a), the more the humic acid added, the less the concentration of available Cu in soil solution was. Humic acid is a kind of organic matter, whose inner structure contains not only abundant benzene ring but also some complex functional groups such as hydroxyl group (-COOH) which can provide electrons to coordinate with heavy metals to form into complex compounds or chelates. The coordination mentioned above is positively related to the concentration of humic acid. Meanwhile, humic acid can easily be adsorbed in the surface of soil colloid. Therefore, adsorption sites in soil particle will increase. It is the combined effects of coordination and adsorption that makes the concentration of available heavy metals decrease in a comparatively large scale [9].

3.2.2. The impact of humic acid on Pb. The ratio of humic acid, pH, temperature all have an obvious impact on the concentration of available Pb in soil. From fig.4, the concentration of available Pb in soil declined when the ratio of humic acid, temperature or pH rose. And, the declining trend was obvious when the ratio of humic acid varied between 3.00% and 5.00%. But, it reached a balance state on the whole under alkaline and high temperature environment.

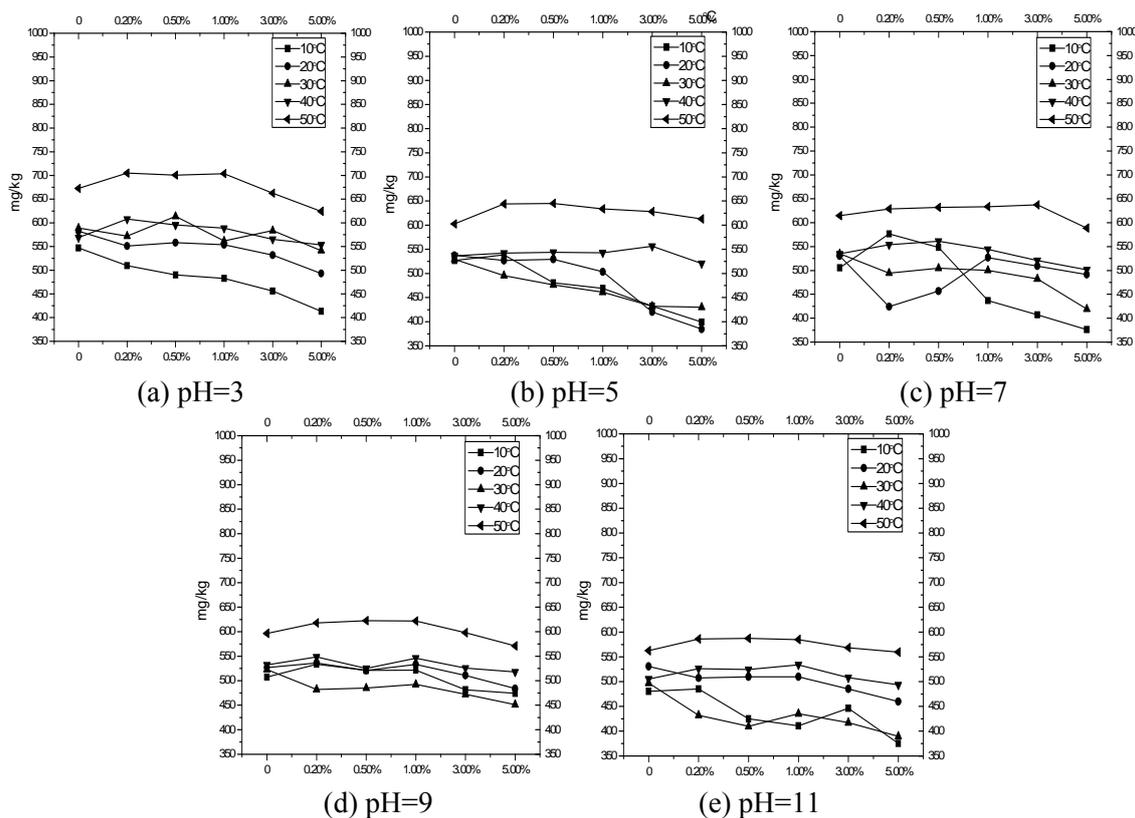


Figure 4. Concentration tendency of available Pb

The ratio of humic acid, pH and temperature both have a certain impact on the removal of available Pb in soil. As is seen from fig.3(b), the removal efficiency was around -10%~30% basically. This rose with more humic acid, lower temperature and lower pH. The best results appeared in 20°C (under acidic or neutral environment), or 30°C (under alkaline environment).

Fig. 3(b) and fig.4 show that, humic acid can efficiently remove Pb in soil, and its mechanism is quite similar to Cu. With the increasing of pH in soil solution, the concentration of available heavy metals dropped. The influence of pH towards the adsorption efficiency of humic acid can be explained in three aspects listed below. Firstly, under lower pH, the dissolution-precipitation equilibrium of Cu, Pb, Cd is destroyed, thus freeing the electrons. In contrast, new dissolution-precipitation equilibrium comes into being under higher pH, thus making the concentration of available heavy metals drop. Secondly, causes of the dropping lie in the tendency to form more carbonate complexes under alkaline environment. Thirdly, more and more humic acid dissolve in soil solution when pH rises, which results in the rising of conditional stability constants between humic acid and Cu, Pb, Cd complexes. This, furtherly results in the reinforcement of their complexing coordination [10].

3.2.3. The impact of humic acid on Cd. The ratio of humic acid and temperature both have a certain impact on the concentration of available Cd in soil while pH shows little influence. Fig.5 shows that on condition that other things being the same, the concentration of available Cd increased when the ratio of humic acid ranging 0~0.20%, however, it dropped when more humic acid added (the ratio gets 5.00%).

As is seen from fig.5, there is no direct relationship between the concentration of humic acid and its adsorption on available Cd. On one hand, the existence of metals ions such as Pb will prevent Cd from binding with adsorption sites of humic acid in soil particle, which is resulted from two main reasons. Firstly, the adsorptive dynamics of soil confirm that the latter adsorbed Pb will replace the former adsorbed Cd. Secondly, law of mass action also may account for this antagonistic action. For the concentration of Pb is much higher than Cd's in mixed contaminated solution, so soil tends to adsorb the higher one, namely, Pb [11]. On the other hand, because the formation of Cd and humic acid is a kind of weak coordination compounds (whose stability constants are smaller than of Pb and Cu), this makes it doesn't have much affinity with solid surface [12].

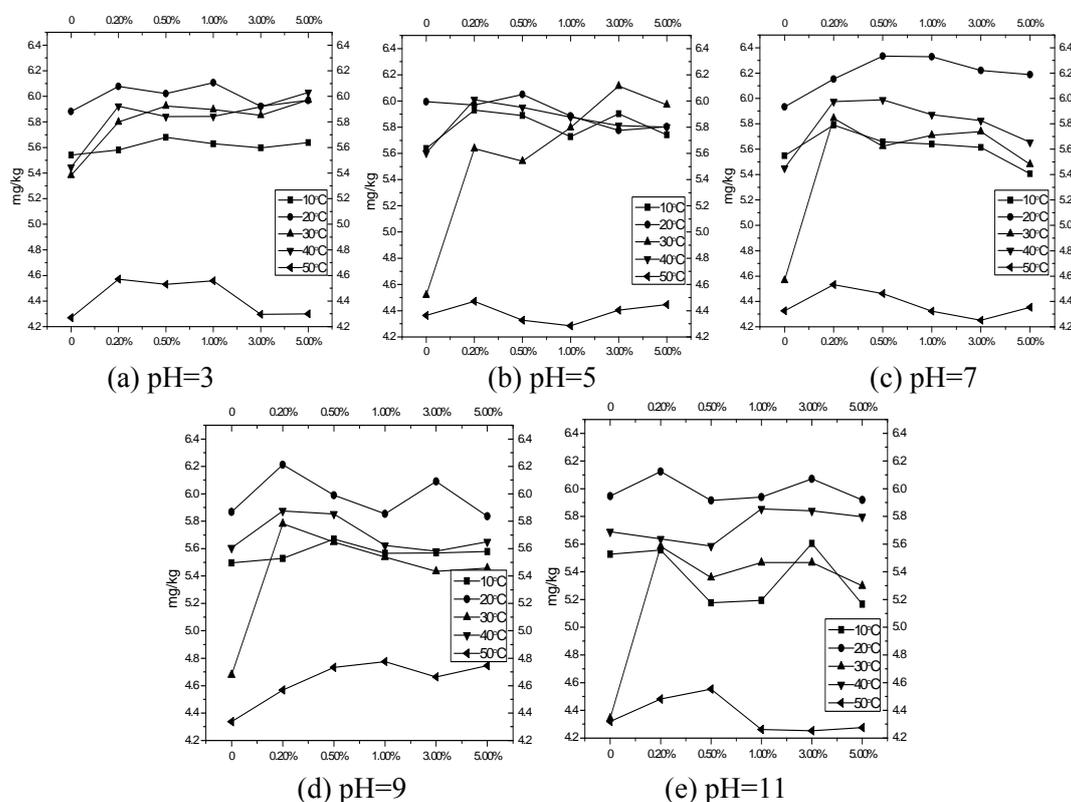


Figure 5. Concentration tendency of available Cd

The removal efficiency of humic acid on available Cd in soil was not ideal. Fig.3(c) shows that humic acid could barely remove available Cd for the highest removal efficiency was just about 5% only in strong alkaline and low temperature environment.

For Cu, its concentration of available fraction reached its peak at 40°C; for Pb, that number was 50°C; and for Cd, it was 20°C. Comparatively speaking, unlike pH and the ratio of humic acid, there is no such thing as regular pattern of the impact of temperature on available heavy metals. This may be explained with the different influence of different temperatures on different heavy metals' activities and the stability of their complexes, which needs a further study to be explained more specific.

3.3. The impact of humic acid on migration rate of Cu, Pb, Cd in contaminated solution

Humic acid has better removal efficiency on heavy metals in contaminated solution. As fig.6 shows, the removal efficiency of humic acid aimed at Cu and Cd could be over 98%. The removal efficiency of Pb even reached 99.996%. However, the counterparts in contaminated soil were 57.283% (Cu), 2.645% (Cd), 15.485% (Pb) respectively. There are competitive absorption and antagonistic action among various heavy metals in contaminated soil while no outside factors will affect the removal efficiency for there only exists single heavy metal in contaminated solution. The existence of competitive ions may influence the adsorption efficiency of humic acid toward Cu^{2+} , Pb^{2+} , Cd^{2+} : the competitive ions are likely to lower the adsorption quantity of themselves firstly, then it is the competition that results in different adsorption amount of each ions. On the contrary, high concentration of Cd^{2+} is able to promote the adsorption of Cu^{2+} instead, which is likely to be the result of the existence of adsorption sites in competition. Therefore, this is shown as preferential adsorption of different adsorbents toward these three ions [13]. Besides, the removal efficiency can be influenced by quite a lot factors (the physicochemical property and composition of soil, the characteristics of heavy metals, etc.), because different property and composition of soil may lead to different adsorption mechanism and form different heavy metal compounds. In the process of adsorptive dynamics, the adsorption of Pb in soil may mainly be the result of ion-exchange reaction and precipitation reaction. However, precipitation reaction may play a major role in the adsorption of Cd [14].

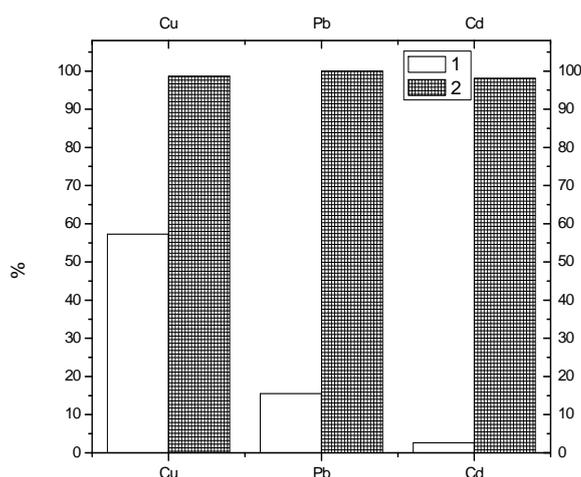


Figure 6. Removal efficiency of available Cu, Pb, Cd in soil (1) and contaminated solution (2)

4. Conclusion

1) Humic acid can effectively lower the concentration of available state of Cu and Pb but slightly influence Cd. The maximal removal efficiency of Cu can reach 57.480%, but 28.372% for Pb and only 6.528% for Cd.

2) pH plays an important role in the stabilizing process of humic acid toward Cu, Pb and Cd in the soil. The rise of pH will cause an obvious decline in the concentration of available heavy metals.

3) Temperature has a certain impact on the stabilizing process of the availability of Cu, Pb and Cd in soil. For instance, when pH=5 and the ratio of humic acid is 5.00%, Cu and Cd get to their maximal removal efficiencies at 10°C, while for Pb it is at 20°C. These differences are possibly caused by different activity and stability of products under different conditions, whose specific mechanisms still need to be further studied.

Acknowledgments

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