

Chemical kinetics and particle size effects of activated carbon for free chlorine removal from drinking water

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Abstract

Activated carbon is an economic material to grab free chlorine in drinking water to reduce potential health risks. In this research, chemical kinetic reaction of the activated carbon for free chlorine removal was studied, which exhibited the first order kinetic reaction performance. A relationship between the rate of chlorinated water flowing through the activated carbon, and the free chlorine (ClO^-) concentrations before and after the reduction by activated carbon was obtained. The logarithm of the free chlorine concentration ($\ln C$) was linearly related to the reciprocal of the volume flow rate ($1/v$). The slope was dependant on the kinetic constant of the activated carbon dechlorination reaction. This research is beneficial for the scientists and engineers to study the mechanism of the chemical kinetic reaction of the free chlorine removal by activated carbon and design activated carbon-loaded water purification reactors.

Key words: activated carbon, free chlorine, kinetic, particle size

INTRODUCTION

Water pollution is one of the critical global hurdles to social progress and threatens public health. To provide clean and safe drinking water through the urban water supply system, water is usually chlorinated to prevent microbial contamination (Yu & Shi 2010). For example, in China, a free chlorine content of $\geq 0.3 \text{ mg L}^{-1}$ after 0.5 h of standing at the end point of an urban water supply system is required (Li *et al.* 2010). However, a high concentration of the chlorine in the drinking water may result in serious health concerns. Due to high chemical activity, the free chlorine prefers to react with various organics and inorganics in drinking water to form a number of chlorinated disinfection by-products (DBPs), including chloramines, chlorates, chlorites, trichlormethane, chloroacetic acid, etc. The DBPs are harmful for people due to properties of carcinogenicity, reproductive toxicity, teratogenicity and mutagenicity (Rossman 2006; Fu *et al.* 2017). Moreover, chloramines are considered to be the sources of chlorinous odour. To effectively reduce the free chlorine in drinking water, many techniques were investigated (Mohammadi *et al.* 2017). A typical one was decomposing the chlorine by ascorbic acid or calcium sulfate through an oxidation-reduction reaction (Ozdemir & Tufekci 1997; Asada *et al.* 2005; Ogata *et al.* 2013). However, the method of oxidation-reduction reaction is impractical due to the high cost of chemical reagents and quantity of chemical waste left at the end of the process. Recently, nanofiltration membrane and reverse osmosis membrane technology has demonstrated a new methodology to remove residual chlorine, including both free chlorine and chlorinated DBPs by separating water and the chlorinated species with an external pressure to overcome osmosis. Although membrane filtration is easy to operate, two drawbacks limit its application. The first is the high cost of the membranes, electricity and pumping equipment. The second

is that the chemical reaction between the chlorine and the membrane expedites membrane aging and shortens membrane life (Zhu & Wang 2017).

Among the available technologies, activated carbon is an efficient and low-cost (\$2.9–9.0/kg) material to remove the free chlorine from drinking water, due to its unique physical and chemical properties, such as large surface area, excellent porosity and safeness (McCreary & Snoeylnk 1981; Sakuma *et al.* 2015; Rasheed *et al.* 2016). The chlorine in water is transported into the pores of the activated carbon by diffusion and physical adsorption. Then, the chlorine is reduced by the activated carbon due to the following two chemical reactions. First, the surface carbon reduces the chlorine to form surface active oxides ($\text{HClO} + \text{C}^* \rightarrow \text{C}^*\text{O} + \text{Cl}^- + \text{H}^+$ and $\text{ClO}^- + \text{C}^* \rightarrow \text{C}^*\text{O} + \text{Cl}^-$; herein, the C^* is the active sites on the activated carbon surface, and the C^*O is the surface oxides). Second, hypochlorous acid (HClO) oxidizes surface carbon to carbon dioxide ($2\text{HClO} + \text{C} \rightarrow 2\text{Cl}^- + 2\text{H}^+ + \text{CO}_2$) (Rossman 2006; Li *et al.* 2010). The chemical reactions between the activated carbon and the chlorine boost the diffusion and the physical adsorption processes and therefore enhance the whole dechlorination process. The dechlorination rate is critical to evaluate the performance of the activated carbon, particularly for activated carbon filter manufacturers. Although the kinetic reaction by activated carbon for chloramines removal was intensively studied (Sakuma *et al.* 2015; Matsushita *et al.* 2017; Skibinski *et al.* 2018), the direct kinetic performance of free chlorine removal by activated carbon was not well understood. Since the free chlorine acts as a precursor to form the chlorinated DBPs, it is of great importance to study the free chlorine removal by activated carbon. In this research paper, kinetic analysis of the dechlorination reaction was studied and used to evaluate the performance of the activated carbon on free chlorine elimination. As far as we know, it is the first time the mathematical relationship between the water flow rate and free chlorine concentration in the water before and after purification by activated carbon has been described. Therefore, this study is beneficial for the understanding of the free chlorine reaction on the surface of activated carbon, and the design of efficient activated carbon-loaded water purification systems.

METHODS

The activated carbon was formed from the carbonation and activation of coconut shells followed by acid-washing (Pushida Inc, Suzhou City, Jiangsu Province, China). The particle size was less than mesh 60 (0.25 mm). The activated carbon was pulverized in a blender with a blade rotation speed of ~20,000 rpm for a few minutes. After pulverization, the activated carbon was sieved to obtain two types of carbon powders according to the particle size (mesh ~50–100 and mesh >80). Therefore, in total, three types of activated carbon were obtained with different particle sizes (Type 1: mesh <60, particle size >0.25 mm; Type 2: mesh ~50–100, particle size 0.30–0.15 mm; Type 3: mesh >80, particle size <0.18 mm). Due to volatility and decomposition of the HClO, NaClO was used to replace the HClO as a chlorine source. The NaClO (Analytic Reagent Grade) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China) with a concentration of effective chlorine >10%. The NaClO was dissolved into de-ionized water with a chlorine concentration of about 1.5 mg L^{-1} (1.5 ppmw), which was stored in a water tank as shown in the fixed-bed reactor schematic in Figure 1. The activated carbon was added to the reactor tube for free chlorine removal. The concentration of the NaClO was tested by using a HACH DR900 spectrometer (Düsseldorf, Germany).

The kinetic free chlorine removal experiments were conducted with the experimental setting in Figure 1. The chlorinated water solution was stored in a water tank (5 L). 4 g of the activated carbon was placed in the reactor for each experiment. At the beginning of each experiment, water valves were opened slightly to let the activated carbon in the reactor be wetted by a small amount of water to squeeze out the gases in the reactor. During the experiments, the reactor was shaken regularly to force the gases generated in the chemical reaction between the chlorine and the activated

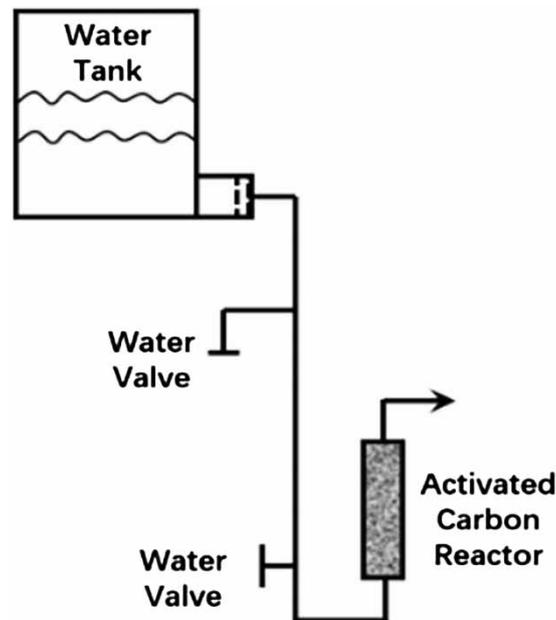


Figure 1 | Schematic of the free chlorine removal reactor.

carbon out of the reactor. Thereafter, the activated carbon was able to be completely saturated by the solution without gas bubbles interfering in the process. The water flow rate was adjusted by the valves and calculated by the water volume being divided by flow time (V/t). The chlorine concentration was measured at the flow rate accordingly.

RESULTS AND DISCUSSION

The hazardous elements in the activated carbon were analyzed by Inductive Coupled Plasma Emission Spectrometer (ICP, Thermo-iCAP6300, Thermo Fisher Scientific, Waltham, MA, USA). The elements content is shown in the [Table 1](#), which met the Standard for Safety Evaluation of Drinking Water Transmission and Distribution Equipment and Protective Materials of China. [Figure 2](#) shows the morphology and composition of the three types of activated carbon. [Figure 2\(a\)–2\(c\)](#) shows the scanning electron microscopy (SEM, Hitachi SU8010, Tokyo, Japan) morphologies of the activated carbon with a magnification of $35\times$. Clearly, the three types of the activated carbon showed different particle sizes of around 0.25–2.00 mm, 0.30–0.15 mm, and <0.18 mm for types 1, 2 and 3 respectively. Energy dispersive spectrometer (EDS) results are shown in [Figure 2\(d\)–2\(f\)](#) with area scanning shown in [Figure 2\(a\)–2\(c\)](#). All three EDS results showed that the particles in the three figures were carbon only without contaminants, which demonstrated similar results to the ICP results in the [Table 1](#).

The isotherms, surface areas and porosity of the activated carbon were analyzed by the Brunauer-Emmett-Teller (BET) adsorption method (Micromeritics, Norcross, GA, USA, ASAP2020 Models). The adsorption-desorption performance and porosity of the activated carbons were demonstrated in [Figure 3](#) to evaluate the physical and chemical performance for the free chlorine removal.

Table 1 | ICP analysis of hazardous items by soaking the activated carbon in water for 24 hr

Element	As	Hg	Mn	Zn
Concentration (mg/L)	<0.005	<0.000028	<0.0005	<0.001
Element	Cd	Pb	Ag	Cr
Concentration (mg/L)	<0.0004	<0.001	<0.002	<0.0019

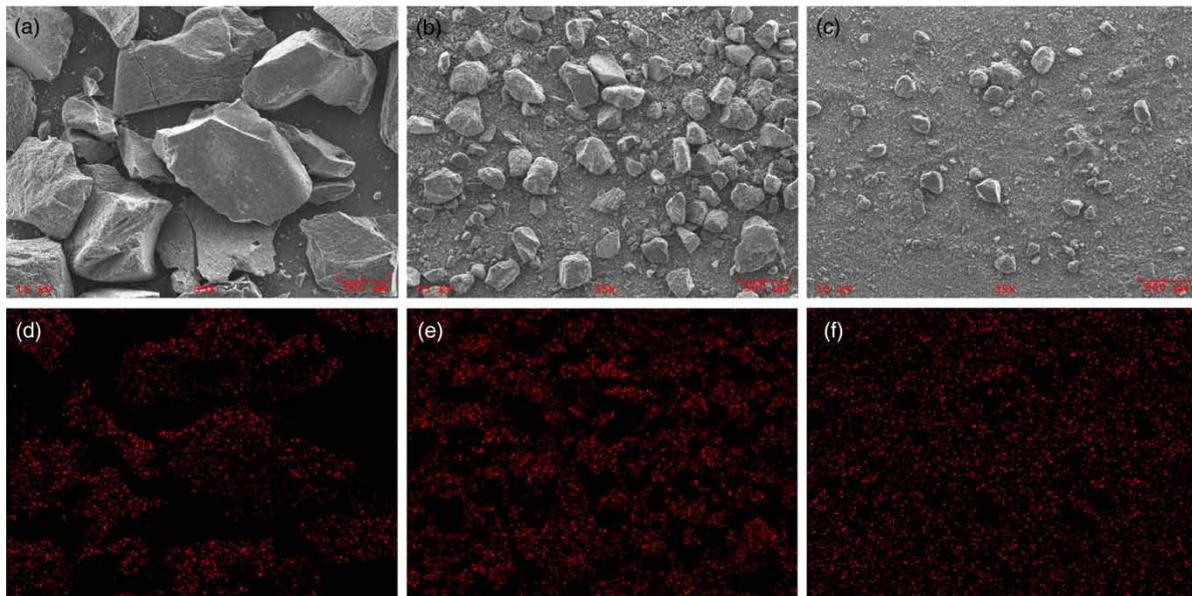


Figure 2 | The type 1, 2 and 3 activated carbon are shown in the SEM images of (a)–(c) respectively. Images (d)–(f) are EDS results of scanning over the areas in the (a)–(c) respectively, with the red areas containing carbon.

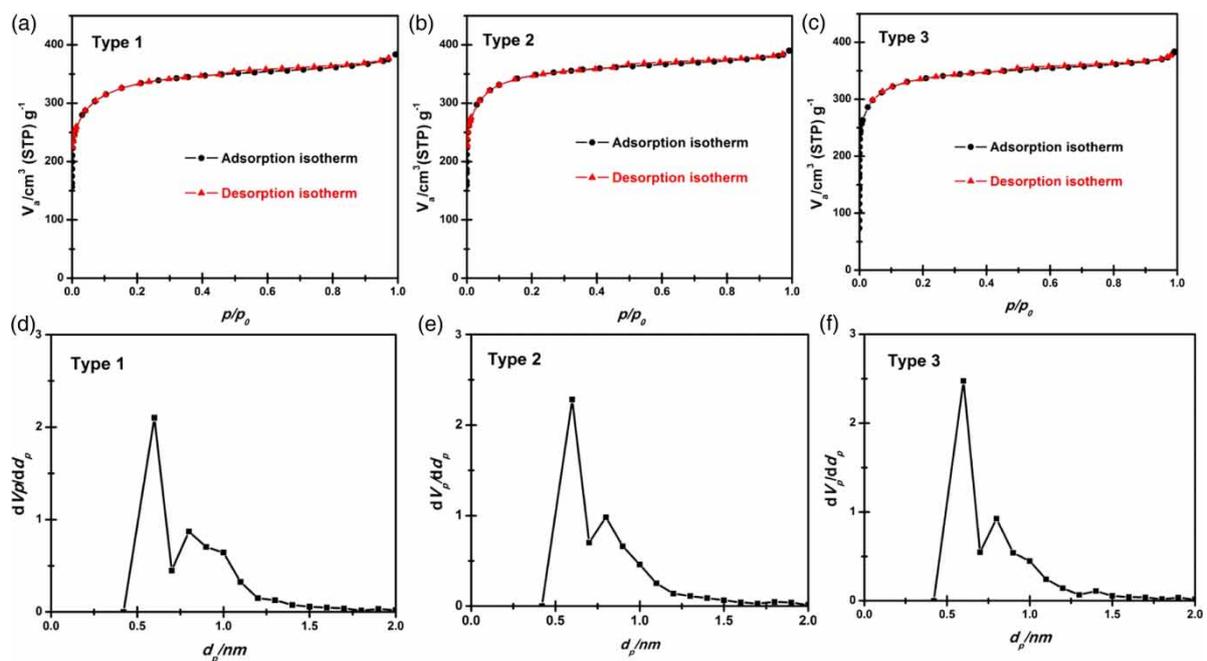


Figure 3 | Nitrogen adsorption-desorption isotherms of the type 1, 2 and 3 activated carbon are shown in figures (a)–(c) respectively. Figures (d)–(f) are micropore size distributions of type 1, 2 and 3 activated carbon respectively.

In Figure 3(a)–3(c), all the three activated carbon types showed similar adsorption-desorption isotherms (I type), indicating micropore-dominated porosity. In addition, the specific surface areas (1,215.9, 1,274.0 and 1,237.8 $\text{m}^2 \text{g}^{-1}$ for types 1, 2 and 3 respectively) and porosity in micropore size (Figure 3(d)–3(f)) of the three types of activated carbon were also similar. Therefore, pulverization cannot change the microstructure of the activated carbon. As can be seen from Figure 3(d)–3(f), the micropores of the activated carbons were mostly in the range of 0.5 to 1.5 nm, which is a good size for free chlorine (ClO^- , HClO , Cl_2) to be adsorbed.

The chlorine in the water reacted with the activated carbon to generate either surface oxides on the activated carbon or carbon dioxide. In either scenario, the oxidizer was HClO or ClO⁻. In this study, the effective chlorine was ClO⁻ because the NaClO acted as a substitution for HClO to avoid fast HClO decomposition. According to classical theory of chemical kinetic reactions, the reaction rate is dependent on the reaction kinetic constant and the reactant concentration. Thus, the free chlorine removal reaction might be described by one of the three following kinetic chemical reaction models according to the reaction order in the differential Equation (1).

$$dC/dt = kC^n, \quad n = 1, 2, \text{ or } 3 \quad (1)$$

Herein, C is the free chlorine concentration in the reactor, t is the contact time, and k is the kinetic constant.

The following three equations can be obtained by integration of the differential Equation (1) with a reaction boundary ($v \rightarrow \infty, C = C_0$), and $t = V/v$ (V is the volume of the water in the activated carbon reactor, and v is the volume rate of water flow).

$$\ln C = kV/v + \ln C_0 \quad (n = 1) \quad (2)$$

$$1/C = -kV/v + 1/C_0 \quad (n = 2) \quad (3)$$

$$1/C^2 = -2kV/v + 1/C_0^2 \quad (n = 3) \quad (4)$$

Herein, C₀ is the chlorine concentration at the inlet of the reactor, and C is the chlorine concentration at the outlet of the reactor.

For the above kinetic equations, lnC, 1/C, and 1/C² are linear with the 1/v as the reaction order n = 1, 2, and 3 respectively. For each type of activated carbon, five data couples of the chlorine concentration after dechlorination and the flow rate were obtained. Then the chlorine concentrations were converted to lnC, 1/C, and 1/C² and linearly fitted, shown in Figures 4–6 respectively. All the fittings were summarized in Table 2. The coefficient of determination (R²) in the first order kinetic reaction fitting were 0.9963, 0.9896, and 0.9904 for the type 1, 2, and 3 activated carbons respectively, which meant a high goodness of fit in the linear regression was independent of the particle size of the activated carbon. However, in Figure 5, Figure 6 and Table 2, the linear relationships of both 1/C vs. 1/v for the second order kinetic reaction and 1/C² vs. 1/v for the third order kinetic reaction showed much smaller R² than that of the lnC vs. 1/v for the first order kinetic reaction. The R² of the second and the third order kinetic reaction fittings in Figures 5 and 6 decreased as the particle size

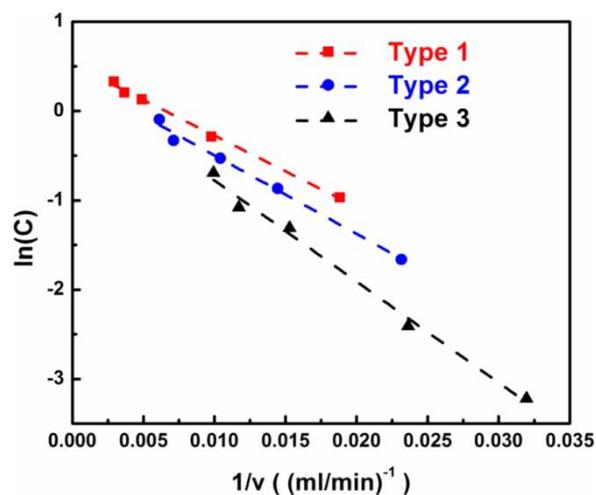


Figure 4 | Linear fitting of the first order kinetic free chlorine removal reaction ($\ln(C) \sim 1/v$) of three types of activated carbon.

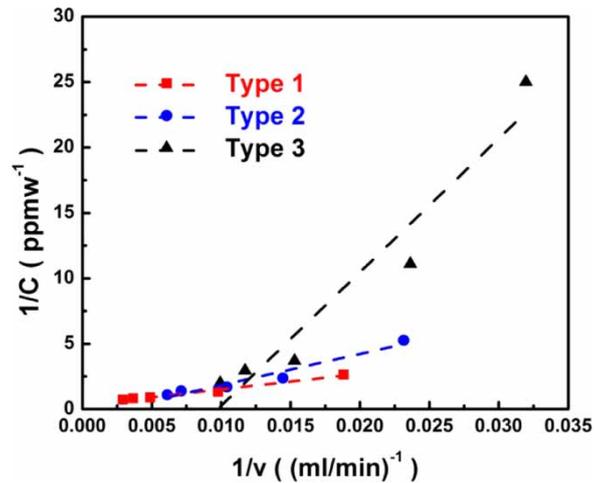


Figure 5 | Linear fitting of the second order kinetic free chlorine removal reaction ($1/C \sim 1/v$) of three types of activated carbon.

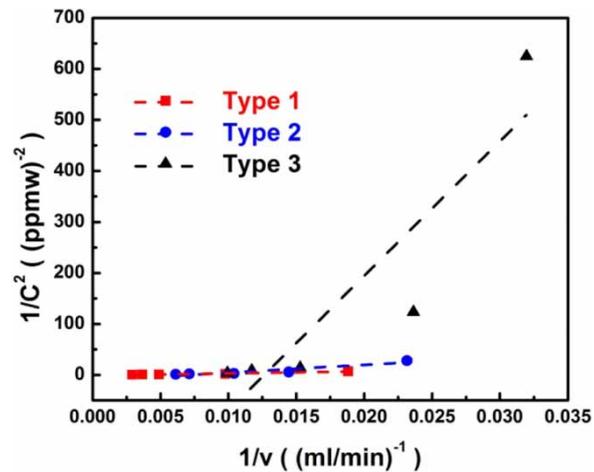


Figure 6 | Linear fitting of the third order kinetic free chlorine removal reaction ($1/C^2 \sim 1/v$) of three types of activated carbon.

Table 2 | Data summary of linear fittings of the three types of activated carbon according to 1, 2, and 3 orders of kinetic free chlorine removal reactions

Linear fitting	Type 1	Type 2	Type 3
First order – slope	-79.89	-87.91	-113.3
First order – intercept	0.523	0.381	0.355
First order – R^2	0.9963	0.9896	0.9904
Second order – slope	119.39	239.08	1021.44
Second order – intercept	0.3177	-0.5641	-9.9544
Second order – R^2	0.9821	0.9414	0.9187
Third order – slope	401.23	1,529.16	26,415.68
Third order – intercept	-1.0869	-10.861	-333.956
Third order – R^2	0.9282	0.8496	0.7620

of the activated carbon increased, indicating that the second and third order kinetic reaction models can not exactly describe the free chlorine removal reaction. In addition, for the first order kinetic reaction model of Equation (2), the intercepts in Table 2 were 0.523, 0.381 and 0.355, indicating the

theoretical chlorine concentrations at the reactor inlet (C_0) of 1.69, 1.46 and 1.43 ppmw for the type 1, 2 and 3 activated carbons respectively. Remarkably, the theoretical C_0 obtained according the first order kinetic reaction model was similar to the experimental concentration $C_0 = 1.5$ ppmw. However, the theoretical C_0 of the second and third kinetic reaction models diverged from the experimental chlorine concentration of 1.5 ppmw significantly. All in all, the first order kinetic reaction is the theoretical model with the highest fitness to describe the free chlorine removal by activated carbon.

In Equation (2), the slope equated to kV . As a constant, V was the volume of the activated carbon, so the slope was dependent on k , the kinetic constant. The plot slopes in Figure 4 and Table 2 increased as the particle size of the activated carbon decreased, demonstrating a higher kinetic constant and a faster free chlorine removal rate of the activated carbon with a smaller particle size. Normally, the reaction rate was related to the specific surface area because reaction sites were anchored onto the surface of the activated carbon. However, both the specific surface area and the porosity of the three types of activated carbon were similar. Therefore, the activated carbon showing a significantly different free chlorine removal rate was not the result of surface area. Actually, most of the dechlorination occurred in the micropores of the activated carbon, which was limited by the diffusion effect of the chlorine. Compared with the activated carbon with a larger particle size, such as types 2 and 3, the activated carbon with a smaller particle size (type 1) offered a higher particle interfacial area, which let the chlorine in the bulk water move into the micropores of the activated carbon much easier. Therefore, more free chlorine molecules diffused from the bulk water into the activated carbon micropores, leading to a higher reaction rate of the free chlorine removal.

CONCLUSIONS

In summary, we used activated carbon with different particle sizes to analyze the performance of free chlorine removal from drinking water. This is the first study to investigate whether the kinetic chemical reaction of free chlorine removal from water by activated carbon follows the theoretical model of first order kinetic reaction. Therefore, a relationship between the water flow rate and the chlorine concentrations before entering and leaving the reactor acted as $\ln C = kV/v + \ln C_0$. The reaction rate was dependent on the kinetic constant k , or the slope kV . This research is beneficial not only for scientists to understand the mechanism of dechlorination by activated carbon, but also for engineers to design more efficient activated carbon filters for free chlorine elimination.

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