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Kinetics of oxidation of manganese by potassium permanganate and chloride in the Velekinca water treatment plant, Kosovo

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Abstract

Our scientific research is based on oxidation reactions and monitoring of chemical reaction kinetics in the Velekinca groundwaters plant in Gjilan municipality, Kosovo. The GW of this plant contains high concentration of manganese so we need to use potassium permanganate (KMnO_4) as one of the most power oxidants in the water treatment plant. In our research the high concentration of Mn in groundwaters is $0.22\text{--}0.28\text{ mg}\cdot\text{dm}^{-3}$ and this concentration is not in accordance with the WHO. Chlorine is one of the most common disinfectants used in the water treatment industry because it has a low cost and immediate effect on the destruction of microorganisms, the concentration of chlorine (Cl_2) in our research is $0.1\text{--}0.32\text{ mg}\cdot\text{dm}^{-3}$. The speed of chemical reactions in the technology of GW is extremely important because sometimes in the elimination of chemical pollutants using oxidizing agents often form intermediate species. The speed of reactions indicates how fast chemical bonds are formed in the creation of a product, and this depends on the rate of reaction (X_A). The focus for the research is to study the potassium permanganate and chlorine gas reactions in water if it forms intermediate products (intermediate species) due to the high speed of reactions. Scientific research conclusion, intermediate species in the oxidation reactions of Mn and water disinfection with $\text{Cl}_{2(g)}$ it is impossible to cause a high rate of chemical reactions from the reaction rate ($X_A = 1\%$) to the reaction rate ($X_A = 99\%$). The maximum speed at the highest $X_A \text{ Cl}_2$ is from $4.405\cdot 10^{-11}$ to $8.87\cdot 10^{-10}\text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$, while at Mn is $(2.030\text{--}4.034)\cdot 10^{-7}\text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$.

Key words: *chemical reactions, chlorine $\text{Cl}_{2(g)}$, groundwater, manganese, oxidation, speed reaction, water treatment plant*

INTRODUCTION

Gjilan is one of the seven largest municipalities in Kosovo. Most of the municipality using groundwaters for drinking water. The Velekinca water plant has six groundwaters with continuous chemical operation. Groundwaters in this water plant needs constant chemical treatment to make drinking water quality, as normal human metabolism.

Groundwater (GW) quality is one of the most sensitive issues worldwide, potentially influenced by several natural and anthropogenic factors. Some of the natural factors include catchment lithology and geology, residence time of groundwater in the rock, pH and ambient temperature,

chemical composition of the aquifer, climatic conditions prevailing during formation, quantity of water available in the aquifer and its rate of circulation and the velocity and direction of water movement [DINKA 2019]. The chemical composition of GW is the product of the long-term interaction between groundwater and the surrounding environment. During the evolution of a groundwater system, different hydrogenochemical processes result in groundwaters having different chemical compositions [BELULI 2019]. However, GW is susceptible to contaminants that need to be removed for the water to be considered safe for consumption [HAKAMI *et al.* 2019]. Manganese ion (Mn^{2+}) is detected commonly in natural aquatic environments, and excessive Mn^{2+} in the water can affect water quality and

human health [GUO *et al.* 2019]. Mn is an essential nutrient yet is toxic at high levels of exposure (Agency for Toxic Substances and Disease Registry – USA) [TOBIASON *et al.* 2016].

Estimation of soil Mn availability has challenged soil scientists since yield increases from Mn fertilization was first demonstrated over 70 years ago [GRAHAM *et al.* 1988]. Manganese reacts with an oxidant agent generating a colloidal precipitate, which is then separated by filtration or sedimentation [REGEANE *et al.* 2013]. Generally, oxidation can be achieved by aeration or chemical oxidation by addition of an oxidising agent such as potassium permanganate (KMnO_4) or chlorine. However, due to fluctuations of manganese levels in raw water, treatment techniques are often very difficult [RAVEENDRAN *et al.* 2002].

Industry automation as opportunity to monitor Cl_2 kinetics and Mn^{2+} oxidation by KMnO_4 : Process control was conducted by developing the apparatus and control devices. Automatic control has advantages because it renders the process independent of human mistakes. To provide a normal progress of industrial processes a sequence of measurements should be conducted with work parameter values. The system that handles this objective, regardless of disturbance that may arise during the development of the process is called the automatic regulation control system [PINGULI *et al.* 2017]. On the other hand, industrial systems are becoming more expensive, which have higher requirements for operation performance, productiveness, availability, reliability, and safety. Moreover, industry has become the current trend of automation industries, which has great impacts on improving the reliability and operation performance of complex industrial systems [GAO *et al.* 2019].

METHODS

Potassium permanganate (KMnO_4). Potassium permanganate is a stronger oxidant than chlorine and sodium hypochlorite. Whilst it is effective in oxidising manganese,

it has also been used for the treatment of taste and odour problems in water supplies. Unlike chlorine, the reaction of KMnO_4 with organic compounds will not produce trihalomethanes, but will actually reduce them. Potassium permanganate is supplied as a powder in 50 kg drums and is mixed on site with water [RAVEENDRAN *et al.* 2002]. In our research KMnO_4 used for the oxidation of Mn as one of the major problems in the groundwater treatment plant in the village of Velekinca in Gjilan etc. The concentration of Mn in the subsoil waters in this plant is from 0.22 to 0.28 $\text{mg}\cdot\text{dm}^{-3}$ [BELULI 2018a]. Manganese is not considered as a frequent element, but in nature, it is quite dispersed. In the crust of soil, it is the tenth element by dispersion [BELULI, MULLIQI 2019]. Therefore, in order to mitigate manganese damage and to ensure a sustainable drinking water supply, development of manganese removing technologies from GW are urgently necessary [ZHANG *et al.* 2017]. High manganese levels in drinking water can give rise to aesthetical and health problems [BUAMAH *et al.* 2009]. Oxidation of Mn poses an engineering challenge, so monitoring not only the amount of water but also in terms of chemical kinetics gives an answer between the reaction path and the effect of reducing the concentration of Mn in water. permanganate

Chlorine (Cl_2). The guidelines for drinking water quality published by World Health Organization (WHO) describes that prevention of waterborne diseases is one of the most important purposes of the water quality control [FUCHIGAMI *et al.* 2010]. Chlorine is the most common disinfectant used in water treatment [SORLINI *et al.* 2015]. In our industrial research, see Figure 1 the water disinfection dose with Cl_2 is 0.1–0.32 $\text{mg}\cdot\text{dm}^{-3}$. In most cases the chlorine of gases in the water industry is judged only in the field of disinfection but on the other hand monitoring the kinetics of chlorine reactions with water enables us to understand more about the formation of products remaining for these inorganic chemical reactions in water and this is facilitated by the kinetics of these reactions with water *etc.*

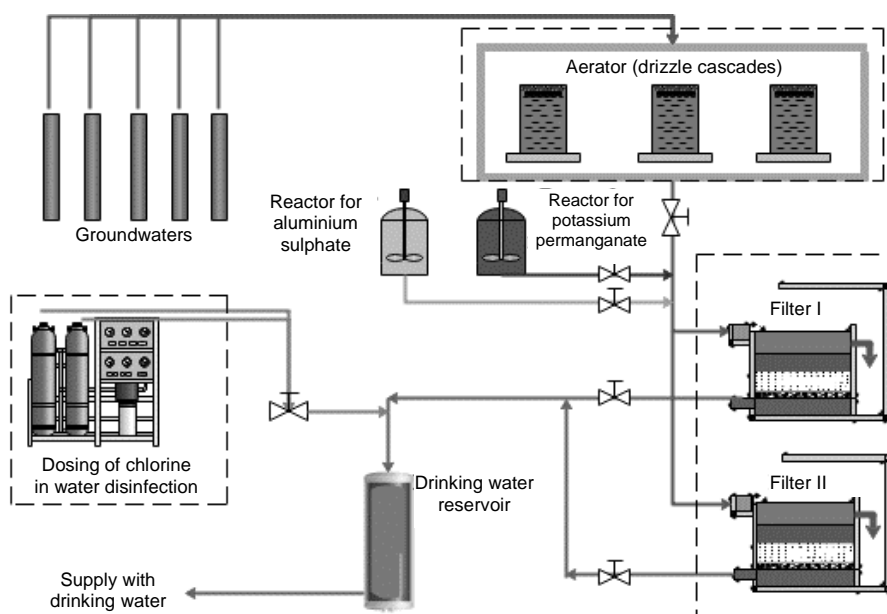


Fig. 1. Industrial process of GW treatment in Velekinca plant in municipality of Gjilan, Kosovo; source: own elaboration

Chemical analyses of manganese and chlorine. The chemical analysis of water is an important complement for the hydrogeological study of the groundwater table, consequently for water resources management. It provides a database on the aquifer environment, the host nature, the supplying and circulation zones in the groundwater table, and the concentration of water pollutants [BEKKOUCH, ZANAGUI 2018].

The HACH® Model DR/2010 Spectrophotometer is a microprocessor-controlled single-beam instrument for colorimetric testing in the laboratory or in the field. The instrument is precalibrated for over 120 different colorimetric measurements and allows convenient calibrations for user entered and future HACH® methods [BELULI 2018a].

Chemical analyses of manganese (Mn). The determination of the concentration of Mn in water in the GW treatment plant was carried out using Spectrophotometer DR/2010 HACH® (PAN-Method 8149, $\lambda = 560$ nm, powder reagent "HACH® Manganese" rank 0–0.700 mg·dm⁻³) [Hach 1999].

Chemical analyses of potassium permanganate (KMnO₄). KMnO₄ was determined according to the analytical methods. 100 cm³ of the sample water was measured into an Erlenmeyer flask (state the capacity) into which 5 cm³ of (state the concentration of the acid) H₂SO₄ was added and heated on an electric heater (state the time) after which 15 cm³ of KMnO₄ was added and further heated on the electric heater for 10 min. Then 15 cm³ of 0.05 mol·dm⁻³ oxalic acid (H₂C₂O₄) was pipetted into the solution and boiled until staining, then titrated with KMnO₄ to a purple colour. The volume in the burette was then read and the mass concentration of KMnO₄ (in mg·dm⁻³) was calculated using Equation (1) [BELULI 2018b]:

$$\text{KMnO}_4 = \frac{[15 + V_{\text{KMnO}_4} - 2 \cdot 15 \cdot \frac{0.05}{5}] \cdot 158.04 \cdot 1000}{V_{\text{Sample}}} \quad (1)$$

Chemical analyses of chlorine (Cl₂). As in other industries the level of automation of drinking water treatment plants has increased up to the level of remote multi-task supervisory control. New process automation software or software updates are tested extensively to prevent dangerous situations [WORM *et al.* 2013]. Chlorine dosing automatically enables us to disinfection water according to European standards. The concentration of chlorine gas in the water can be measured through HACH® internal sensors where the concentration of Cl_{2(g)} is present in the operating room of the water plant (Photo 1).

Measurements of the speeds of chemical reactions. A very important unit of a chemical reaction in which we took interest is the scale of substance conversion that takes part in the reaction. The scale of conversion of a compound that participates in the chemical reaction is the ratio of the number of moles that have been converted during the reaction and the initial number of moles, as seen in Table 1 [MALOLLARI, PINGULI 2014].



Photo 1. Automatic dosage and monitoring of chlorine concentration in water for disinfection and monitoring the kinetics of water reactions (phot. V. Beluli)

Table 1. Measurements of the speeds of chemical reactions formulas

Parameter	Formula
C_A – substance concentration	$C_A = C_{A0} - C_{A0} \cdot X_A$
C or C_{A0} – concentration	$C = m/V \cdot M$
S – density	$S = m/V$
r_A – speed of chemical reaction	$r_A = \frac{C_{A0} - C_A}{V \cdot t_0}$

Explanations: C_A = substance concentration after a time interval (mol·dm⁻³), C_{A0} = initial substance concentration of the reaction (mol·dm⁻³), X_A = scale of reaction, C or C_{A0} = concentration (mol·dm⁻³), m = amount of substance used for solution preparation in a chemical reactor (g), V = volume of chemical reactor (dm³), M = relative molecular mass (kg·mol⁻¹), r_A = speed of chemical reaction (mol·dm⁻³·s⁻¹), C_{A0} = concentration of initial reaction substance, C_A = concentration of substance after a time interval, V = volume of water flow (dm³·s⁻¹), t_0 = flow of gas chlorine or KMnO₄ (dm³·s⁻¹).

Source: MALOLLARI, PINGULI [2014].

RESULTS AND DISCUSSION

DESCRIBING SPEED (r_A) OF Cl_{2(g)} IN PROPORTION TO THE SCALE OF CONCENTRATION (C_{A0}).

Cl_{2(g)} has a high reaction speed with water, as seen in Table 2, the faster the reactant concentration decreases, the more speed is increased. Diagram of the following study as in (Fig. 2) proves that near the first half of the chemical reaction, [H₂O-Cl-Cl] bonding starts, and in the second half of the reaction, H⁺ ion detaches from the water molecule by forming the unstable bonds [HO-Cl-Cl]⁻. These bonds do not hold for too long because of the unstable state, Cl⁻ ion (aq) detaches and forms HOCl + H⁺ as seen in Figure 2. According to obtained results Cl_{2(g)} is highly reactive in room temperature. The theory of crash of atoms is highly present in the reaction of water chlorination when the concentration of chlorine in water is high. The higher the quantity of Cl₂ in water, the greater the collision of atoms. Chemical reaction theory has proven scientifically that gas atoms must have an orderly geometrical structure in order for the collisions to be direct, because when the atoms don't have orderly geometry the collisions start to evade and as a result the chemical reaction speed starts to decrease. In our research the chemical reaction speed has been measured in a second and it results that the theory of

Table 2. Reaction speed (r_A) of Cl_2 (g) including dosage concentration 0.1–0.45 $\text{mg}\cdot\text{dm}^{-3}$, scale of reaction (X_A) and concentration of reactant (C_A)

X_A (%)	C_{A0} ($\text{mol}\cdot\text{dm}^{-3}$)	C_A ($\text{mol}\cdot\text{dm}^{-3}$)	r_A ($\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$)	X_A (%)	C_{A0} ($\text{mol}\cdot\text{dm}^{-3}$)	C_A ($\text{mol}\cdot\text{dm}^{-3}$)	r_A ($\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$)
0.10 $\text{mg}\cdot\text{dm}^{-3}$				0.16 $\text{mg}\cdot\text{dm}^{-3}$			
1	$1.410 \cdot 10^{-6}$	$1.39 \cdot 10^{-6}$	$4.406 \cdot 10^{-12}$	1	$2.256 \cdot 10^{-6}$	$2.23 \cdot 10^{-6}$	$1.128 \cdot 10^{-12}$
10		$1.26 \cdot 10^{-6}$	$4.406 \cdot 10^{-12}$	10		$2.03 \cdot 10^{-6}$	$1.128 \cdot 10^{-11}$
20		$1.40 \cdot 10^{-4}$	$8.812 \cdot 10^{-12}$	20		$1.80 \cdot 10^{-6}$	$2.256 \cdot 10^{-11}$
30		$9.87 \cdot 10^{-7}$	$1.321 \cdot 10^{-11}$	30		$1.57 \cdot 10^{-6}$	$3.384 \cdot 10^{-11}$
40		$8.46 \cdot 10^{-7}$	$1.762 \cdot 10^{-11}$	40		$1.35 \cdot 10^{-6}$	$4.512 \cdot 10^{-11}$
50		$7.05 \cdot 10^{-7}$	$2.203 \cdot 10^{-11}$	50		$1.12 \cdot 10^{-6}$	$5.640 \cdot 10^{-11}$
60		$5.64 \cdot 10^{-7}$	$2.643 \cdot 10^{-11}$	60		$9.02 \cdot 10^{-6}$	$6.768 \cdot 10^{-11}$
70		$4.23 \cdot 10^{-7}$	$3.084 \cdot 10^{-11}$	70		$6.76 \cdot 10^{-6}$	$7.896 \cdot 10^{-11}$
80		$2.82 \cdot 10^{-7}$	$3.525 \cdot 10^{-11}$	80		$4.61 \cdot 10^{-7}$	$9.024 \cdot 10^{-11}$
90		$1.41 \cdot 10^{-7}$	$3.965 \cdot 10^{-11}$	90		$2.25 \cdot 10^{-7}$	$1.015 \cdot 10^{-10}$
99.99		$1.00 \cdot 10^{-9}$	$4.405 \cdot 10^{-11}$	99.99		$1.00 \cdot 10^{-9}$	$1.127 \cdot 10^{-10}$
0.20 $\text{mg}\cdot\text{dm}^{-3}$				0.30 $\text{mg}\cdot\text{dm}^{-3}$			
1	$2.820 \cdot 10^{-6}$	$2.791 \cdot 10^{-6}$	$1.762 \cdot 10^{-12}$	1	$4.231 \cdot 10^{-6}$	$4.188 \cdot 10^{-6}$	$3.966 \cdot 10^{-12}$
10		$2.538 \cdot 10^{-6}$	$1.762 \cdot 10^{-12}$	10		$3.807 \cdot 10^{-6}$	$3.966 \cdot 10^{-11}$
20		$2.256 \cdot 10^{-6}$	$3.525 \cdot 10^{-11}$	20		$3.807 \cdot 10^{-6}$	$3.966 \cdot 10^{-11}$
30		$1.974 \cdot 10^{-6}$	$5.287 \cdot 10^{-11}$	30		$2.962 \cdot 10^{-6}$	$1.189 \cdot 10^{-10}$
40		$1.692 \cdot 10^{-6}$	$7.050 \cdot 10^{-11}$	40		$2.538 \cdot 10^{-6}$	$1.586 \cdot 10^{-10}$
50		$1.410 \cdot 10^{-6}$	$8.812 \cdot 10^{-11}$	50		$2.115 \cdot 10^{-6}$	$1.983 \cdot 10^{-10}$
60		$1.128 \cdot 10^{-6}$	$1.057 \cdot 10^{-10}$	60		$1.692 \cdot 10^{-6}$	$2.379 \cdot 10^{-10}$
70		$8.460 \cdot 10^{-7}$	$1.233 \cdot 10^{-10}$	70		$1.269 \cdot 10^{-6}$	$2.776 \cdot 10^{-10}$
80		$5.640 \cdot 10^{-7}$	$1.410 \cdot 10^{-10}$	80		$8.462 \cdot 10^{-7}$	$3.173 \cdot 10^{-10}$
90		$2.820 \cdot 10^{-7}$	$1.586 \cdot 10^{-10}$	90		$4.231 \cdot 10^{-7}$	$3.569 \cdot 10^{-10}$
99.99		$5.410 \cdot 10^{-7}$	$1.424 \cdot 10^{-10}$	99.99		$5.000 \cdot 10^{-10}$	$3.966 \cdot 10^{-10}$
0.31 $\text{mg}\cdot\text{dm}^{-3}$				0.32 $\text{mg}\cdot\text{dm}^{-3}$			
1	$4.372 \cdot 10^{-6}$	$4.328 \cdot 10^{-6}$	$4.235 \cdot 10^{-12}$	1	$4.513 \cdot 10^{-6}$	$4.467 \cdot 10^{-6}$	$4.513 \cdot 10^{-12}$
10		$3.895 \cdot 10^{-6}$	$4.192 \cdot 10^{-11}$	10		$4.061 \cdot 10^{-6}$	$4.513 \cdot 10^{-11}$
20		$3.462 \cdot 10^{-6}$	$8.385 \cdot 10^{-11}$	20		$3.610 \cdot 10^{-6}$	$9.026 \cdot 10^{-11}$
30		$3.029 \cdot 10^{-6}$	$1.257 \cdot 10^{-10}$	30		$3.159 \cdot 10^{-6}$	$1.353 \cdot 10^{-10}$
40		$2.597 \cdot 10^{-6}$	$1.677 \cdot 10^{-10}$	40		$2.711 \cdot 10^{-6}$	$1.805 \cdot 10^{-10}$
50		$2.164 \cdot 10^{-6}$	$2.096 \cdot 10^{-10}$	50		$2.256 \cdot 10^{-6}$	$2.256 \cdot 10^{-10}$
60		$1.732 \cdot 10^{-6}$	$2.515 \cdot 10^{-10}$	60		$1.805 \cdot 10^{-6}$	$2.707 \cdot 10^{-10}$
70		$1.298 \cdot 10^{-6}$	$2.934 \cdot 10^{-10}$	70		$1.353 \cdot 10^{-6}$	$3.159 \cdot 10^{-10}$
80		$8.656 \cdot 10^{-7}$	$3.354 \cdot 10^{-10}$	80		$9.026 \cdot 10^{-7}$	$3.610 \cdot 10^{-10}$
90		$3.895 \cdot 10^{-6}$	$3.773 \cdot 10^{-10}$	90		$4.513 \cdot 10^{-7}$	$4.060 \cdot 10^{-10}$
99.99		$1.000 \cdot 10^{-9}$	$4.192 \cdot 10^{-10}$	99.99		$1.000 \cdot 10^{-9}$	$4.512 \cdot 10^{-10}$
0.35 $\text{mg}\cdot\text{dm}^{-3}$				0.37 $\text{mg}\cdot\text{dm}^{-3}$			
1	$4.936 \cdot 10^{-6}$	$4.886 \cdot 10^{-6}$	$5.395 \cdot 10^{-12}$	1	$5.218 \cdot 10^{-6}$	$5.165 \cdot 10^{-6}$	$6.126 \cdot 10^{-12}$
10		$4.442 \cdot 10^{-6}$	$5.395 \cdot 10^{-11}$	10		$4.696 \cdot 10^{-6}$	$6.032 \cdot 10^{-11}$
20		$3.948 \cdot 10^{-6}$	$1.079 \cdot 10^{-10}$	20		$4.113 \cdot 10^{-6}$	$1.205 \cdot 10^{-10}$
30		$3.455 \cdot 10^{-6}$	$1.618 \cdot 10^{-10}$	30		$3.652 \cdot 10^{-6}$	$1.810 \cdot 10^{-10}$
40		$2.962 \cdot 10^{-10}$	$2.158 \cdot 10^{-10}$	40		$3.130 \cdot 10^{-6}$	$2.412 \cdot 10^{-10}$
50		$2.468 \cdot 10^{-6}$	$2.697 \cdot 10^{-10}$	50		$2.609 \cdot 10^{-6}$	$3.016 \cdot 10^{-10}$
60		$1.974 \cdot 10^{-6}$	$3.237 \cdot 10^{-10}$	60		$2.087 \cdot 10^{-6}$	$3.619 \cdot 10^{-10}$
70		$1.481 \cdot 10^{-6}$	$3.776 \cdot 10^{-10}$	70		$1.566 \cdot 10^{-6}$	$4.221 \cdot 10^{-10}$
80		$9.872 \cdot 10^{-7}$	$4.316 \cdot 10^{-10}$	80		$1.044 \cdot 10^{-6}$	$4.825 \cdot 10^{-10}$
90		$4.936 \cdot 10^{-7}$	$4.855 \cdot 10^{-10}$	90		$5.218 \cdot 10^{-10}$	$5.428 \cdot 10^{-10}$
99.99		$5.000 \cdot 10^{-10}$	$5.394 \cdot 10^{-10}$	99.99		$6.000 \cdot 10^{-10}$	$6.031 \cdot 10^{-10}$
0.40 $\text{mg}\cdot\text{dm}^{-3}$				0.45 $\text{mg}\cdot\text{dm}^{-3}$			
1	$5.641 \cdot 10^{-6}$	$5.584 \cdot 10^{-6}$	$7.125 \cdot 10^{-12}$	1	$6.340 \cdot 10^{-4}$	$6.270 \cdot 10^{-6}$	$9.800 \cdot 10^{-12}$
10		$5.641 \cdot 10^{-7}$	$7.051 \cdot 10^{-11}$	10		$5.706 \cdot 10^{-6}$	$8.876 \cdot 10^{-11}$
20		$4.512 \cdot 10^{-6}$	$1.411 \cdot 10^{-10}$	20		$5.072 \cdot 10^{-6}$	$1.775 \cdot 10^{-10}$
30		$3.949 \cdot 10^{-6}$	$2.115 \cdot 10^{-10}$	30		$4.438 \cdot 10^{-6}$	$2.662 \cdot 10^{-10}$
40		$3.385 \cdot 10^{-6}$	$2.820 \cdot 10^{-10}$	40		$3.804 \cdot 10^{-6}$	$3.550 \cdot 10^{-10}$
50		$2.820 \cdot 10^{-6}$	$3.526 \cdot 10^{-10}$	50		$3.170 \cdot 10^{-6}$	$4.438 \cdot 10^{-10}$
60		$2.257 \cdot 10^{-6}$	$4.230 \cdot 10^{-10}$	60		$2.536 \cdot 10^{-6}$	$5.325 \cdot 10^{-10}$
70		$1.693 \cdot 10^{-6}$	$2.116 \cdot 10^{-10}$	70		$1.902 \cdot 10^{-6}$	$6.213 \cdot 10^{-10}$
80		$1.129 \cdot 10^{-6}$	$5.640 \cdot 10^{-10}$	80		$1.268 \cdot 10^{-6}$	$7.100 \cdot 10^{-10}$
90		$5.920 \cdot 10^{-7}$	$6.311 \cdot 10^{-10}$	90		$6.340 \cdot 10^{-7}$	$7.988 \cdot 10^{-10}$
99.99		$1.000 \cdot 10^{-9}$	$7.050 \cdot 10^{-10}$	99.99		$1.000 \cdot 10^{-9}$	$8.870 \cdot 10^{-10}$

Source: own study.

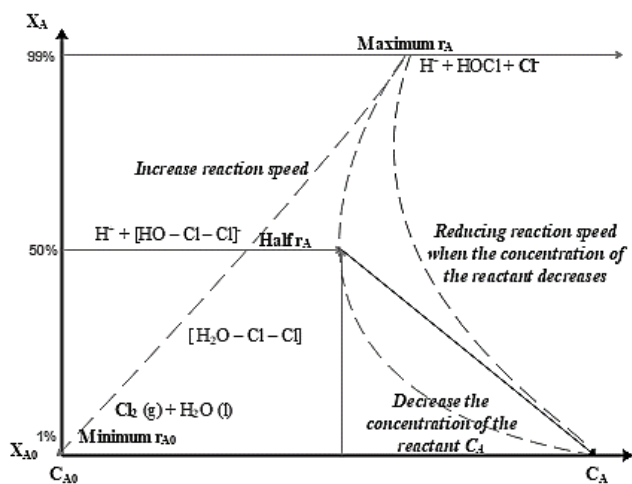


Fig. 2. Description of reaction speed of $\text{Cl}_{2(\text{g})}$ through the scale of reaction ($X_{A0}-X_A$) and the concentration of reactants ($C_{A0}-C_A$) in formation of the final product $\text{Cl}^-_{(\text{aq})}$; source: own study

crash among gas atoms has been very high, fast and efficient and this is seen in the obtained results in Table 2. We have monitored the intake quantity of water from GW springs by observing the increase of chlorine in water depending on the intake of water at the treatment plant.

The higher the intake of water, the higher the dosage of $\text{Cl}_{2(\text{g})}$. For experimental kinetic studies we have used chlorine concentration from $0.1 \text{ mg}\cdot\text{dm}^{-3}$ to $0.45 \text{ mg}\cdot\text{dm}^{-3}$.

REACTION SPEED (R_A) OF $\text{KMnO}_{4(\text{AQ})}$ IN PROPORTION WITH THE SCALE OF CONCENTRATION (C_{A0}) AND SCALE OF REACTION (X_A)

KMnO_4 is a chemical substance which is using quite a lot in Mn oxidation, as a heavy metal is toxic in water. Firstly, KMnO_4 is dissolved into a 750 dm^3 chemical reactor and is well mixed before dissolving completely, then the mixer works continually at low speeds and also the dosage of KMnO_4 in water becomes automatic by monitoring the concentration of Mn in groundwaters. Dissolution of

Table 3. Reaction speed of Mn oxidation with KMnO_4 including digestive concentration of KMnO_4 700–1500 g in chemical reactor of 750 dm^3 , scale of reaction (X_A), and the concentration of reactant (C_A)

X_A (%)	C_{A0} ($\text{mol}\cdot\text{dm}^{-3}$)	C_A ($\text{mol}\cdot\text{dm}^{-3}$)	r_A ($\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$)	X_A (%)	C_{A0} ($\text{mol}\cdot\text{dm}^{-3}$)	C_A ($\text{mol}\cdot\text{dm}^{-3}$)	r_A ($\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$)
700 g				800 g			
1	$5.905\cdot 10^{-3}$	$5.845\cdot 10^{-3}$	$2.031\cdot 10^{-9}$	1	$6.752\cdot 10^{-3}$	$6.683\cdot 10^{-3}$	$2.153\cdot 10^{-9}$
10		$5.314\cdot 10^{-3}$	$2.031\cdot 10^{-8}$	10		$6.075\cdot 10^{-3}$	$2.153\cdot 10^{-8}$
20		$4.724\cdot 10^{-3}$	$4.062\cdot 10^{-8}$	20		$5.400\cdot 10^{-3}$	$4.306\cdot 10^{-8}$
30		$4.134\cdot 10^{-3}$	$6.093\cdot 10^{-8}$	30		$4.725\cdot 10^{-3}$	$6.459\cdot 10^{-8}$
40		$3.603\cdot 10^{-3}$	$8.124\cdot 10^{-8}$	40		$4.050\cdot 10^{-3}$	$8.612\cdot 10^{-8}$
50		$2.953\cdot 10^{-3}$	$1.015\cdot 10^{-7}$	50		$3.375\cdot 10^{-3}$	$1.076\cdot 10^{-7}$
60		$2.362\cdot 10^{-3}$	$1.218\cdot 10^{-7}$	60		$2.700\cdot 10^{-3}$	$1.291\cdot 10^{-7}$
70		$1.772\cdot 10^{-3}$	$1.421\cdot 10^{-7}$	70		$2.025\cdot 10^{-3}$	$1.507\cdot 10^{-7}$
80		$1.181\cdot 10^{-3}$	$1.624\cdot 10^{-7}$	80		$1.350\cdot 10^{-3}$	$1.722\cdot 10^{-7}$
90		$5.905\cdot 10^{-4}$	$1.827\cdot 10^{-7}$	90		$6.751\cdot 10^{-3}$	$1.937\cdot 10^{-7}$
99.99	$1.000\cdot 10^{-6}$	$2.030\cdot 10^{-7}$	99.99	$6.751\cdot 10^{-7}$	$2.152\cdot 10^{-7}$		
900 g				1000 g			
1	$7.594\cdot 10^{-3}$	$7.518\cdot 10^{-3}$	$2.143\cdot 10^{-9}$	1	$8.438\cdot 10^{-3}$	$8.354\cdot 10^{-3}$	$2.833\cdot 10^{-9}$
10		$6.834\cdot 10^{-3}$	$1.926\cdot 10^{-7}$	10		$7.594\cdot 10^{-3}$	$2.833\cdot 10^{-8}$
20		$6.075\cdot 10^{-3}$	$4.405\cdot 10^{-8}$	20		$6.751\cdot 10^{-3}$	$5.666\cdot 10^{-8}$
30		$5.315\cdot 10^{-3}$	$6.422\cdot 10^{-8}$	30		$5.907\cdot 10^{-3}$	$8.500\cdot 10^{-8}$
40		$4.556\cdot 10^{-3}$	$8.562\cdot 10^{-8}$	40		$5.063\cdot 10^{-3}$	$1.133\cdot 10^{-7}$
50		$3.797\cdot 10^{-3}$	$1.070\cdot 10^{-7}$	50		$4.219\cdot 10^{-3}$	$1.416\cdot 10^{-7}$
60		$3.037\cdot 10^{-3}$	$1.284\cdot 10^{-7}$	60		$3.375\cdot 10^{-3}$	$1.700\cdot 10^{-7}$
70		$2.278\cdot 10^{-3}$	$1.498\cdot 10^{-7}$	70		$2.531\cdot 10^{-3}$	$1.983\cdot 10^{-7}$
80		$1.518\cdot 10^{-3}$	$1.712\cdot 10^{-7}$	80		$1.687\cdot 10^{-3}$	$2.266\cdot 10^{-7}$
90		$7.594\cdot 10^{-4}$	$1.926\cdot 10^{-7}$	90		$8.438\cdot 10^{-4}$	$2.550\cdot 10^{-7}$
99.99	$8.000\cdot 10^{-7}$	$2.140\cdot 10^{-7}$	99.99	$8.438\cdot 10^{-7}$	$2.833\cdot 10^{-7}$		
1200 g				1500 g			
1	$1.0126\cdot 10^{-2}$	$1.002\cdot 10^{-2}$	$3.533\cdot 10^{-7}$	1	$1.265\cdot 10^{-2}$	$1.252\cdot 10^{-2}$	$4.305\cdot 10^{-9}$
10		$9.113\cdot 10^{-3}$	$3.376\cdot 10^{-8}$	10		$1.138\cdot 10^{-2}$	$4.305\cdot 10^{-8}$
20		$8.100\cdot 10^{-3}$	$6.750\cdot 10^{-8}$	20		$1.012\cdot 10^{-2}$	$4.356\cdot 10^{-9}$
30		$7.088\cdot 10^{-4}$	$3.139\cdot 10^{-7}$	30		$8.855\cdot 10^{-3}$	$1.291\cdot 10^{-7}$
40		$6.075\cdot 10^{-3}$	$1.350\cdot 10^{-7}$	40		$7.590\cdot 10^{-3}$	$1.722\cdot 10^{-7}$
50		$5.063\cdot 10^{-3}$	$1.687\cdot 10^{-7}$	50		$6.325\cdot 10^{-3}$	$2.152\cdot 10^{-7}$
60		$4.050\cdot 10^{-3}$	$2.025\cdot 10^{-7}$	60		$5.060\cdot 10^{-3}$	$2.583\cdot 10^{-7}$
70		$3.037\cdot 10^{-3}$	$2.362\cdot 10^{-7}$	70		$3.795\cdot 10^{-3}$	$3.013\cdot 10^{-7}$
80		$2.025\cdot 10^{-3}$	$2.700\cdot 10^{-7}$	80		$2.530\cdot 10^{-3}$	$3.444\cdot 10^{-7}$
90		$1.012\cdot 10^{-3}$	$3.037\cdot 10^{-7}$	90		$1.265\cdot 10^{-3}$	$3.874\cdot 10^{-7}$
99.99	$1.013\cdot 10^{-6}$	$3.374\cdot 10^{-7}$	99.99	$1.265\cdot 10^{-6}$	$4.034\cdot 10^{-7}$		

Source: own study.

$\text{KMnO}_{4(\text{aq})}$ in the reactor includes concentration 700–1500 g in 750 dm^3 . As a main process in this industry KMnO_4 dosage in water before filtration. The chemical reaction speed of Mn oxidation as a heavy metal is very high. We have proved that when the concentration of KMnO_4 is high then also the speed of the chemical reaction is high, refer to Table 3. Mn oxidation has no transitory state as Cl_2 oxidation, here, the reaction is fast and almost immediately changing Mn into MnO_2 , as in Figure 3 and this is a reason why KMnO_4 is extensively using in water plant.

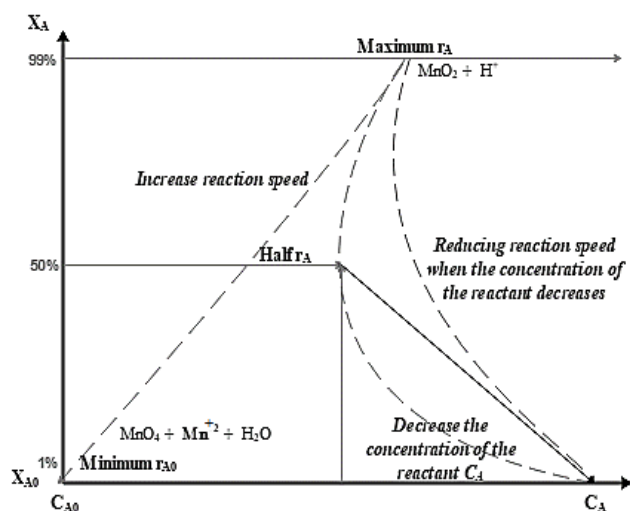


Fig. 3. Description of reaction speed of Mn oxidation with KMnO_4 (s) through the scale of reaction (X_{A0} – X_A) and the concentration of reactants (C_{A0} – C_A) in forming of the final product MnO_2 (aq); source: own study

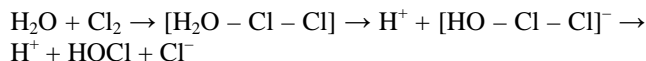
Finding reaction pathways is the most important task in the theoretical study on the mechanism of chemical reactions. Hence, reaction pathways have been calculated in numerous theoretical studies. The most frequently calculated reaction path is the intrinsic reaction coordinate [MAEDA *et al.* 2013].

Cl_2 dosage in water has been presented in Figure 4A. Characteristic of halogen redox reactions is disproportionality, which is favourable by thermodynamics for basic solution of Cl_2 . Disproportionality is much less favourable

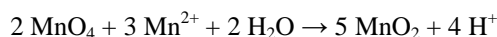
by thermodynamics in acidic solution, being obvious by the fact that H^+ ions are produced by the reaction [ATKINS *et al.* 2006]:



The mechanism of this reaction seems to include the attacking of H_2O molecule into the Cl_2 molecule:



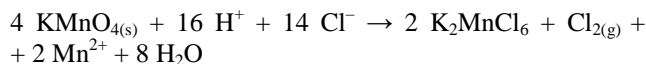
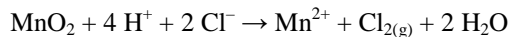
This includes considering where chemicals are added in the treatment process, the order in which they are injected and how chemical feed rates are controlled [SHODHAN, WEI 2010]. Only manganese forms very stable compounds with oxidation scale +2. Mn^{2+} ions are also present in water solutions of Mn (II) compounds. Although Mn^{2+} is a rare element, it is quite spread all over the nature. It is the tenth ranked element by percentage in earth's crust, more than other metals except for iron (Fe). This ion can be oxidized in compounds with higher scales of oxidation only under the influence of strong oxidizing agents Figure 4B. For example, ion MnO_4^- oxidizes Mn^{2+} into MnO_2 as in the following reaction [BELULI *et al.* 2018b]:



So, Mn^{3+} ion oxidizes the present anion. If the anion cannot be oxidized then Mn^{3+} oxidizes itself widely in water solutions and comes to the disproportion of that ion:



So MnO_2 oxidizes the chloride ion into molecular chlorine:



In these reactions it is very difficult to form half products during the development of chemical reactions because the detachment of bonds is formation of new chemical bonds between molecules is very fast: X_A 99%, r_A $(2.030\text{--}4.034) \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ and the rate of chemical reaction for chlorine is: X_A 99%, r_A from $4.405 \cdot 10^{-11}$ to $4.512 \cdot 10^{-10} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$.

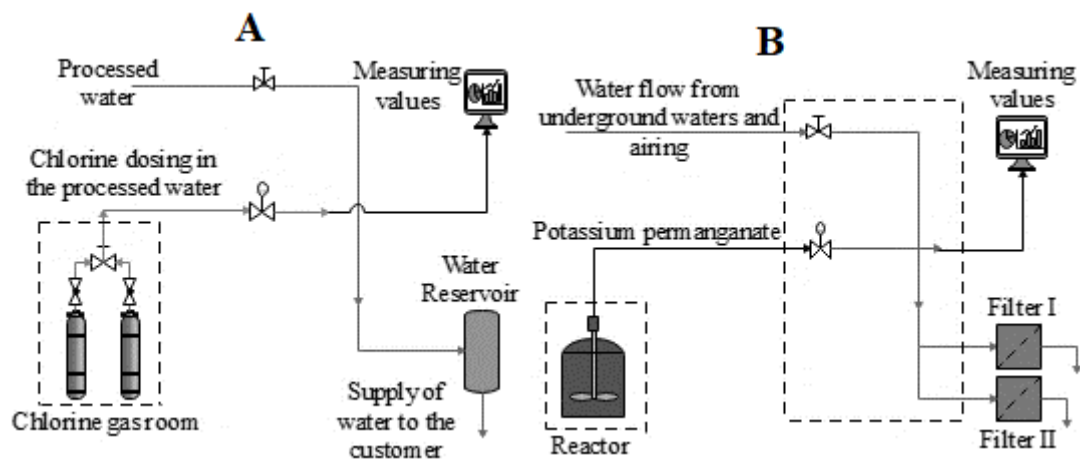


Fig. 4. (A) The room of chlorine (Cl_2) dosage in water after filtering groundwaters (B) Water solution dosage with KMnO_4 for Mn oxidation before water filtration; source: own study

CONCLUSIONS

The speed of the chemical reaction is one of the most important theories in modern chemistry for the development of chemical reactions. Without chemical and physical factors many times reactions have been unrealizable. It has been proven scientifically that the speed of the chemical reactions of water chlorination and manganese oxidation is very high. The termination of these reactions in forming products has been really fast as explained in above diagrams regarding our two important reactions. According to our scientific research in these reactions it is very hard to form half products during the development of chemical reactions because the detachment of bonds is formation of new chemical bonds between molecules is very fast: X_A 99%, r_A $(2.030-4.034) \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$. During water chlorination in summer season, $\text{Cl}_{2(g)}$ dosage is a higher quantity because of the higher temperatures and the rate of chemical reaction is: X_A 99%, r_A from $4.405 \cdot 10^{-11}$ to $4.512 \cdot 10^{-10} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$. Mn oxidation as a heavy metal present in many groundwaters, during summer season Mn as a metal is greatly reduced, while during winter season when rainfall increases, then the consecration of Mn in these groundwaters many times it is not in accordance with the WHO and European regulations for direct water consumption. If the concentration of KMnO_4 is increasing then the oxidation of Mn is much faster as seen in the tables above. During this scientific research we have proved that the chemical reaction speed of Mn oxidation with KMnO_4 is much faster rather than the reaction with $\text{Cl}_{2(g)}$.

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