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Marta Pyrih, Zenovii Znak

RESEARCH ON THE EFFICIENCY OF THE MnO_2/CLINOPTILOLITE COMPOSITE SYNTHESIZED UNDER MICROWAVE RADIATION IN THE PROCESSES OF WATER PURIFICATION FROM Fe^{2+} IONS

Lviv Polytechnic National University, Lviv, Ukraine

The composite of MnO_2/clinoptilolite nanoparticles was synthesized by impregnating natural clinoptilolite with a solution of $Mn(NO_3)_2$ with subsequent decomposition of $Mn(NO_3)_2$ under microwave electromagnetic radiation (radiation frequency: 2.45 GHz; power: 500 W). EDX analysis showed that doping of clinoptilolite with manganese occurs both due to ion exchange and adsorption from the $Mn(NO_3)_2$ solution, and the manganese content in the surface and near-surface layers of clinoptilolite particles was also determined. The effect of pH and temperature on the rate of oxidation of Fe^{2+} ions in model $FeSO_4$ solutions with an initial Fe^{2+} concentration of 5±0.1 mg/L in a column was investigated using the native form of clinoptilolite and the synthesized MnO_2/clinoptilolite composite. It was found that the rate of oxidation of Fe^{2+} in the presence of the native form of clinoptilolite is very low. At the same time, in the case of using the MnO_2/clinoptilolite composite, the oxidation rate is one to two orders of magnitude higher. It was found that the pH of the medium has the greatest influence on the course of oxidation of Fe^{2+} ions. For example, at pH 8.5 and a temperature of 20^0C, the time required for complete oxidation of iron(II) ions is no more than 70 s.

Keywords: clinoptilolite, modification, MnO_2 particles, iron(II) ions, water purification, oxidation.

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Introduction

The quality of natural surface waters in Ukraine often does not meet regulatory standards. In many cases, this is due to damage or destruction of the infrastructure of municipal water utilities: treatment plants, water canals, pumping stations, fresh water supply and wastewater disposal networks, as well as critical damage or destruction of hydraulic structures (dams, weirs, reservoirs) damaged by russian aggression [1–5]. For example, the destruction of the Kakhovka hydroelectric power station caused a massive discharge of water and the displacement of bottom sediments, in which heavy metals had accumulated for decades, which sharply increased the risk of contamination of groundwater and soil in the runoff and infiltration zones [6]. In view of the above, the involvement of new water resources in the water supply of the population of Ukraine is increasingly relevant. These include, in particular, natural groundwater and mine waters, which are currently not used due to the presence of impurities that make them impossible to use directly for consumption. These include, in particular, iron compounds.

Therefore, the purification of the above-mentioned

militarily contaminated, underground, mine and other waters is relevant. Given the very large needs for water supply, it is very important to find effective, cheap and technologically simple methods for conditioning contaminated natural waters. The simplest methods for removing iron(II) compounds are oxidation with air oxygen [7,8]. But these waters contain a complex of pollutants of different phase-dispersion composition (dissolved (for example, iron(II) compounds), highly dispersed and colloidal particles). Therefore, purification methods that combine several purification processes are effective, for example, separation of dispersed particles, removal of iron(II) compounds [9]. Sorption methods that use sorbents of various nature, on which iron ions are simultaneously oxidized due to the significant area of contact of oxygen with water [10,11]. At the same time, a complex effect in water purification processes is provided by sorbents modified with compounds that give them additional functional properties [12]. In particular, for water purification from iron(II) ions, it is advisable to use sand, ceramics, zeolites modified with manganese(IV) oxide, which has catalytic-oxidative properties [13,14]. Most often, manganese(IV) oxide is deposited on a support using potassium permanganate as a precursor, the use of which is associated with formal difficulties [13]. Therefore, a method for the deposition of manganese oxides on natural clinoptilolite using ultrasonic and electromagnetic radiation was developed [15,16].

The purpose of this work is to establish the efficiency of oxidation of iron(II) ions using MnO_2 deposited on natural clinoptilolite as a result of the decomposition of manganese nitrate under the influence of microwave electromagnetic radiation.

Experimental

To obtain the MnO_2/clinoptilolite composite, zeolite (clinoptilolite) from the Sokyrnytsia deposit (Transcarpathian region, Ukraine) was used. Natural clinoptilolite was pre-enriched by physical methods: during grinding and by washing clay impurities with water under intensive stirring. After washing and drying to a constant mass at room temperature (this achieves the natural moisture content), a clinoptilolite fraction with sizes of 1.0−1.5 mm was separated. Clinoptilolite modification was carried out as a two-stage process. At the first stage, clinoptilolite was impregnated with a 0.5 M solution of $Mn(NO_3)_2$ at a mass ratio of solid and liquid phases of 1:4 with constant stirring and under the action of acoustic radiation in the ultrasonic (US) range. To generate ultrasonic radiation, an ultrasonic emitter «Ultrasonic Disintegrator UD-20» was used (frequency: 20 kHz, power: 10.2 W). Modification was carried out under isothermal conditions at a temperature of 25±0.5^{0}C for 30 min. During this time, sorption equilibrium was practically reached, as evidenced by the practically constant concentration of Mn^{2+} ions in the modification solution. The concentration of Mn^{2+} ions was determined complexometrically. Modified clinoptilolite was separated from the solution by filtration under vacuum.

At the second stage, wet clinoptilolite impregnated with a $Mn(NO_3)_2$ solution was transferred to a quartz glass, which was placed in the resonator chamber of a Samsung microwave oven (radiation frequency: 2.45 GHz, power: 500±25 W). Under the influence of ultrahigh-frequency electromagnetic radiation, $Mn(NO_3)_2$ decomposed with the formation of dispersed particles of manganese oxide and the release of a characteristic brown gas (NO_2) directly in the quartz glass:

$$Mn(NO_3)_2=MnO_2+2NO_2.$$

MnO_2 particles gave the clinoptilolite particles a color ranging from dark brown to almost black. The difference in color is due to the uneven composition of natural clinoptilolite particles.

Morphological analysis of the surface of modified clinoptilolite, as well as the content of manganese and exchangeable cations (Na, K, Ca, and Mg) in the surface layers of zeolite particles, which are contained in natural clinoptilolite, was carried out by energy-dispersive X-ray spectroscopy (EDX) using an INCA Energy 350 device (Oxford Instruments), integrated into the Zeiss EVO-40XVP scanning electron microscope system.

To study the efficiency and regularities of the oxidation of Fe^{2+} ions using the synthesized MnO_2/clinoptilolite composite, a $FeSO_4$ solution with a concentration of 5.0±0.1 mg/L was passed through a glass column filled with the MnO_2/clinoptilolite composite from the bottom up (Fig. 1).

Air was also bubbled through the solution in the column to ensure oxidation of Fe^{2+} ions. The column was equipped with a system of fittings located at different heights to sample the solution for Fe^{2+} ions at different residence times in the column. These data were used to establish the dependence of the Fe^{2+} ion concentration on time.

To establish the effectiveness of MnO_2 as an oxidation catalyst, parallel studies were conducted using the same clinoptilolite fraction, but in its native form, i.e., not modified.

To avoid premature oxidation of Fe^{2+} ions, the $FeSO_4$ solution was prepared by dissolving a portion of $FeSO_4{\cdot}7H_2O$ in distilled water, from which dissolved oxygen was first removed by boiling. The pH value of the $FeSO_4$ solution, which was controlled using a pH

meter, was adjusted by dosing 0.01 M solutions of H_2SO_4 or NaOH. The lower pH value of 5.5 corresponds to the acidity of many types of groundwater, and the upper pH value of 8.5 is the permissible value according to regulatory documents.

The content of Fe^{2+} ions in the solution was determined spectrophotometrically according to DSTU ISO 6332:2003 (ULab-102 spectrophotometer) at 510 nm using 1,10-phenenthroline as an indicator.

Results and discussion

The EDX method established that during the treatment of natural clinoptilolite with a solution of $Mn(NO_3)_2$, ion exchange occurs: exchangeable cations of clinoptilolite are exchanged for Mn^{2+} ions from the solution (Fig. 2).

That is, there is selectivity of ion exchange in the studied system. First, Na^+ and Mg^{2+} ions are exchanged; they are exchanged almost completely, therefore they are absent from the EDX spectrum. To a lesser extent, K^+ and Ca^{2+} ions are exchanged. Their content in modified clinoptilolite (in the surface layers) is 0.74 and 0.42 wt.%. At the same time, the manganese content reaches even 56 wt.%. Therefore, it can be assumed that the absorption of Mn^{2+} ions occurs not only due to ion exchange, but also due to the sorption of $Mn(NO_3)_2$ from the modification solution.

At a low initial pH value of 5.5, the initial rate of oxidation of Fe^{2+} ions is very low even when using modified clinoptilolite (Fig. 3a). In the case of unmodified clinoptilolite, an increase in temperature from 10 to 20^{0}C has practically no effect on the rate of oxidation of Fe^{2+} ions (Fig. 3a, curves 1–3). The presence of MnO_2 on the surface of clinoptilolite causes an increase in the rate of oxidation of Fe^{2+} ions. Thus, at a temperature of 20^{0}C, the initial rate of oxidation is higher, compared to unmodified clinoptilolite at temperatures of 10–30^{0}C and modified at 15 and 20^{0}C, by 190, 2.4 and 1.52 times, respectively. That is, in the presence of MnO_2, the rate of oxidation of Fe^{2+} is higher by approximately 2 orders of magnitude.

Increasing the pH of the medium causes an increase in the oxidation rate of Fe^{2+} ions (Fig. 3). Thus, an increase in pH from 5.5 to 6.5 causes an increase in the initial oxidation rate by approximately an order of magnitude in all cases (Fig. 3b). At pH≈7.0, the initial oxidation rate for the native form of clinoptilolite increases by 2.8, 4.7, and 6.5 times at temperatures of 10, 15, and 20^{0}C, respectively. At the same time, in the case of modified clinoptilolite, a different trend is observed: the initial rate of the process at temperatures of 10, 25, and 20^{0}C increases by 7.1, 5.3, and 4.3 times, respectively. Such results can be explained by the oxidation of Fe^{2+} with the formation of $Fe(OH)_3$, the particles of which somewhat block the surface of MnO_2 particles on clinoptilolite. This conclusion is confirmed by the dependence of the initial oxidation rate on pH with its further increase. However, no clear pattern of increase in oxidation rate from pH values at the specified temperatures was found. For example, the increase in the process rate

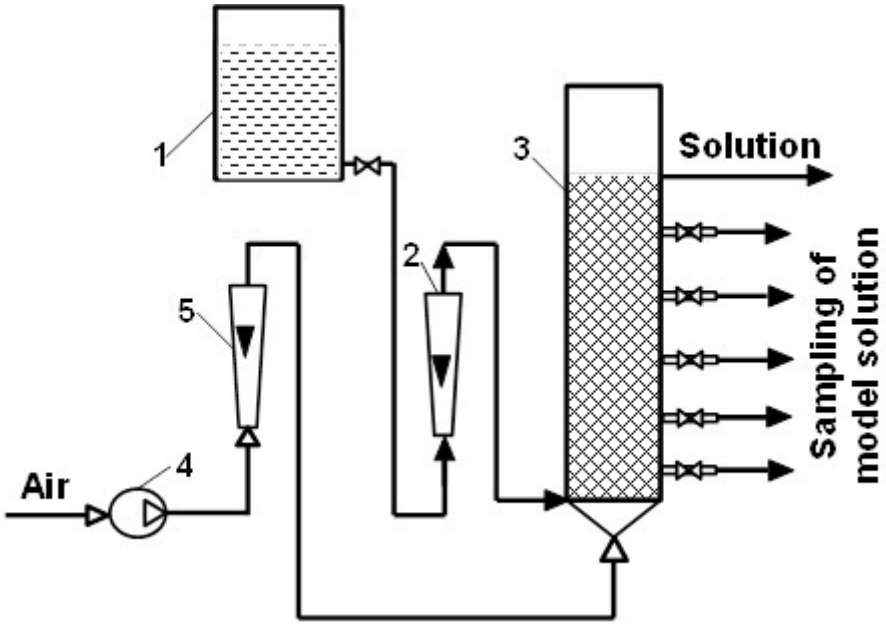

Fig. 1. Scheme of a laboratory setup for studying the purification of model water from Fe^{2+} ions: 1 – tank with model solution; 2, 5 – rotameters; 3 – column with clinoptilolite or MnO_2/clinoptilolite composite; 4 – compressor

at pH 8.5 compared to 7.5 is 1.6, 1.3 and 1.7 times, respectively, at the specified temperatures. This is probably due to the heterogeneity of the shape of natural clinoptilolite particles, heterogeneity of size and heterogeneity of distribution of MnO_2 particles on clinoptilolite, and the formation of $Fe(OH)_3$.

The significant influence of the pH value of the medium on the rate of oxidation of Fe^{2+} ions is due to the following main factors: (1) with an increase in pH, Fe^{2+} forms hydroxo complexes $Fe(OH)^+$, which are more reactive, while at lower pH, less reactive aqua complexes are formed; (2) the formation of poorly soluble $Fe(OH)_3$, due to which the equilibrium in the Fe^{2+}—Fe^{3+} system shifts towards the formation of Fe^{3+}, i.e. a decrease in the concentration of Fe^{2+}; and (3) an increase in the rate of oxidation by dissolved oxygen [17].

The values of the oxidation rate constant of iron(II) ions under various conditions are given in Table.

The value of the Van't Hoff temperature coefficient (γ) calculated for processes involving the MnO_2/clinoptilolite composite at temperatures of 10 and 20^{0}C at pH of the medium of 5.5, 6.5, 7.0, 7.5 and 8.0 is 2.0, 1.7, 2.5, 4.6 and 4.4, respectively. For the process of oxidation of Fe^{2+} ions involving the MnO_2/clinoptilolite composite, the activation energy values are within 41.7—54.5 kJ/mol (with the exception of only one case at pH 6.5). The obtained data indicate that the process of oxidation of Fe^{2+} ions occurs in the kinetic region. However, an increase in temperature in the case of deironing of groundwater, the temperature of which is usually not more than 15^{0}C, is not economically feasible.

The decisive influence of the pH of the solution on the oxidation of Fe^{2+} ions is demonstrated by the dependence of the duration of the process until almost complete oxidation of Fe^{2+}. For example, when using the MnO_2/clinoptilolite composite at a temperature of 20^{0}C, the degree of oxidation of Fe^{2+} ions of 100% at pH 5.5, 6.5, 7.0, 7.5 and 8.5 is achieved approximately within 3.8 h, 1.1 h, 20 min, 120 s and 70 s, respectively. At a temperature of 15^{0}C, this time is approximately equal to 4.9 h (determined by calculation), 1.6 h, 42 min, 140 s and 90 s. When performing calculations, it is practically impossible to take into account the participation of iron(III) compounds, which are formed as a result of the oxidation of Fe^{2+} ions and can also catalyze the oxidation of Fe^{2+}, as well as the blocking of active catalytic centers on the surface of modified clinoptilolite by poorly soluble iron(III) compounds in oxidation processes.

Therefore, the composite of MnO_2/clinoptilolite nanoparticles synthesized by the decomposition of manganese nitrate under the action of microwave radiation can be used as an effective filter loading for water purification from dispersed particles and soluble iron(II) compounds.

Conclusions

Using the EDX method, the manganese content on the surface and in the near-surface layers of the modified clinoptilolite particles was determined, reaching 56 wt.%. Modification with manganese occurs

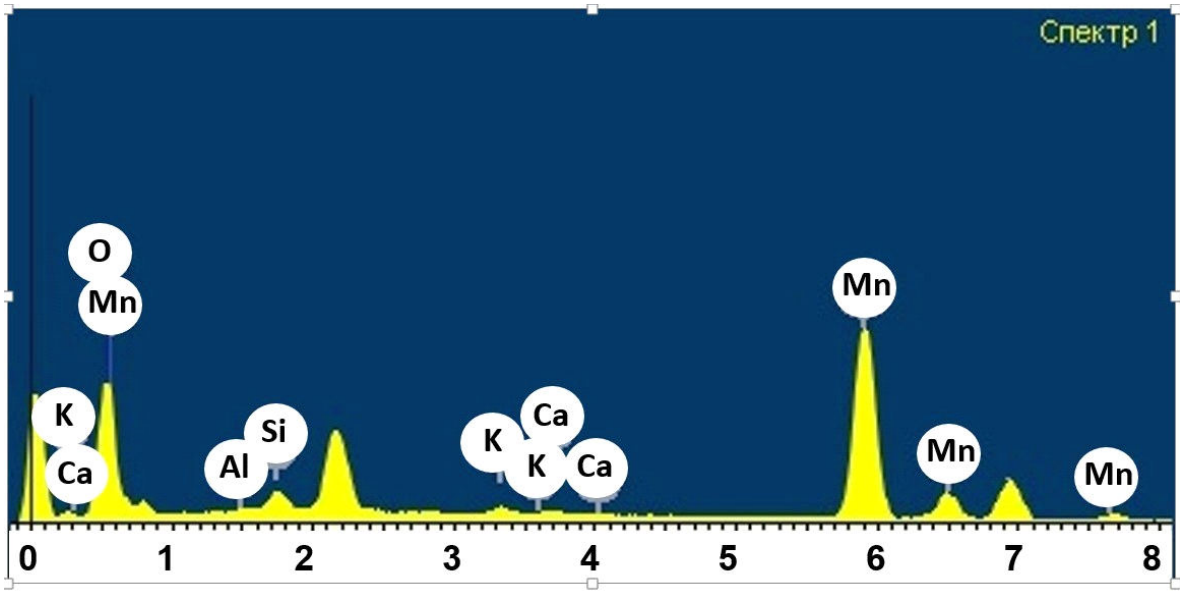

Fig. 2. EDX spectrum of the MnO_2/clinoptilolite nanoparticle composite obtained by decomposition in a microwave electromagnetic field

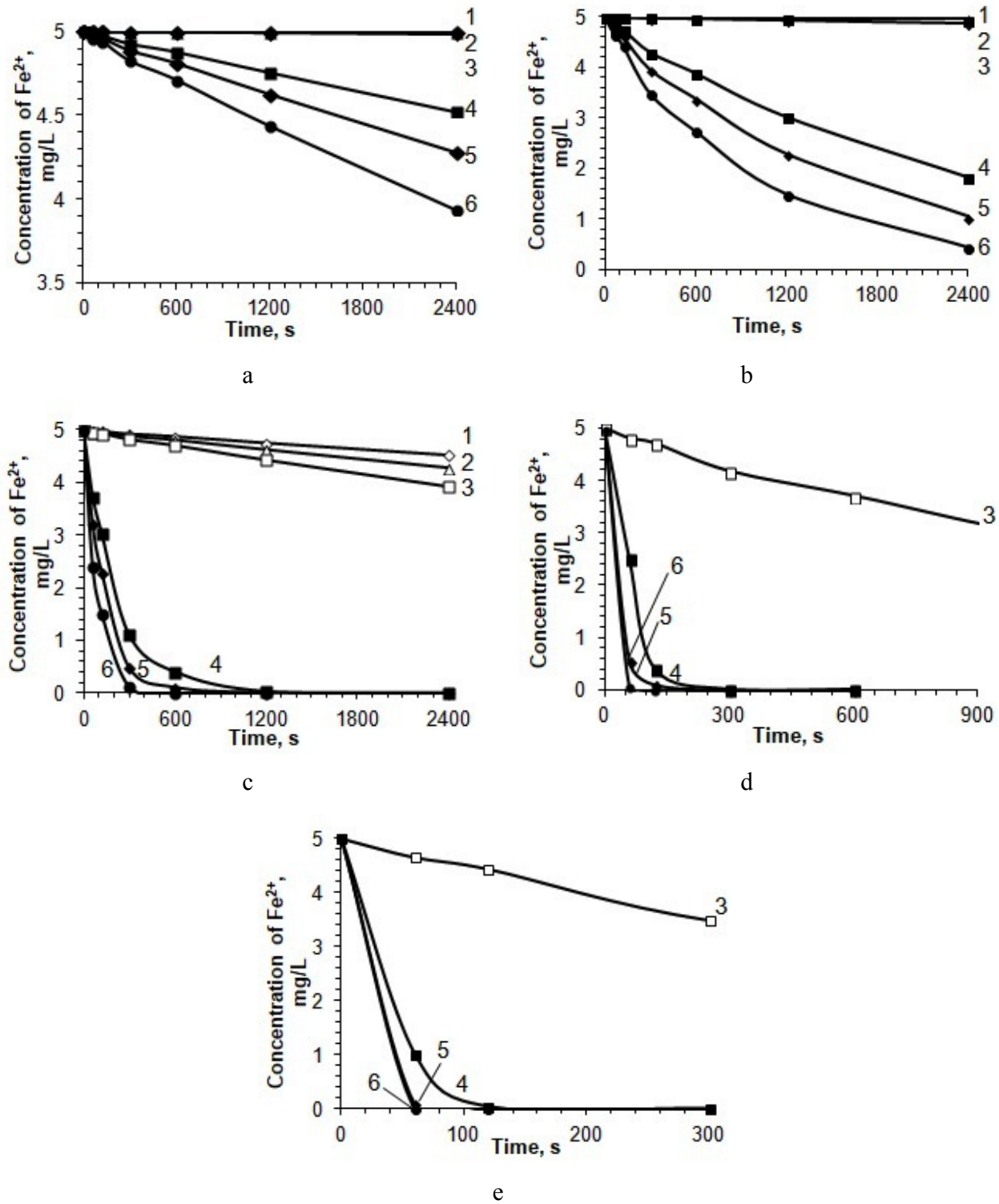

Fig. 3. Dependence of Fe^{2+} ion concentration on time under the following conditions: pH:
a – 5.5; b – 6.5; c – 7.0; d – 7.5; e – 8.5; temperature: 1 and 4 – 10^0C; 2 and 4 – 15^0C; 3 and 6 – 20^0C

due to ion exchange and sorption of the $Mn(NO_3)_2$ solution.

The oxidation of Fe^{2+} ions, in particular with the participation of the MnO_2/clinoptilolite composite, occurs mainly in the kinetic region, which is confirmed by both the values of the Van't Hoff temperature coefficient ($\gamma \geq 2$) and the activation energy value (E_a=41.7−54.5 kJ/mol).

Doping clinoptilolite with manganese(IV) oxide contributes to an increase in the rate constant of the oxidation of Fe^{2+} ions by two orders of magnitude.

The greatest influence on the rate and, accordingly, the value of the rate constant has the pH of the medium: in particular, with an increase in pH from 5.5 to 8.5, the value of the rate constant of Fe^{2+} oxidation at temperatures of 10 and 15^0C increases by three orders of magnitude.

Natural clinoptilolite, doped with MnO_2 particles according to the developed method, is a promising filter material for effective water purification from iron(II) compounds.

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The values of the oxidation rate constant of Fe^{2+} ions

pH	Rate constant, s^{-1}					
	temperature					
	10^0C		15^0C		20^0C	
	clinoptilolite form					
	native	with MnO_2	native	with MnO_2	native	with MnO_2
5.5	$4.190 \cdot 10^{-7}$	$3.337 \cdot 10^{-5}$	$6.520 \cdot 10^{-7}$	$6.680 \cdot 10^{-5}$	$1.000 \cdot 10^{-6}$	$1.339 \cdot 10^{-4}$
6.5	$4.190 \cdot 10^{-6}$	$6.804 \cdot 10^{-4}$	$6.520 \cdot 10^{-6}$	$4.390 \cdot 10^{-4}$	$1.000 \cdot 10^{-5}$	$1.138 \cdot 10^{-3}$
7.0	$4.190 \cdot 10^{-5}$	$4.839 \cdot 10^{-3}$	$1.000 \cdot 10^{-4}$	$7.386 \cdot 10^{-3}$	$1.340 \cdot 10^{-4}$	$1.216 \cdot 10^{-2}$
7.5	$2.090 \cdot 10^{-4}$	$1.475 \cdot 10^{-2}$	$3.370 \cdot 10^{-4}$	$3.679 \cdot 10^{-2}$	$6.800 \cdot 10^{-4}$	$6.792 \cdot 10^{-2}$
8.5	$4.190 \cdot 10^{-4}$	$2.682 \cdot 10^{-2}$	$6.460 \cdot 10^{-4}$	$6.696 \cdot 10^{-2}$	$1.210 \cdot 10^{-3}$	$1.188 \cdot 10^{-1}$

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ДОСЛІДЖЕННЯ ЕФЕКТИВНОСТІ КОМПОЗИТУ MnO_2/КЛИНОПТИЛОЛІТ, СИНТЕЗОВАНОГО ПІД ДІЄЮ НВЧ-ВИПРОМІНЮВАННЯ, У ПРОЦЕСАХ ОЧИЩЕННЯ ВОДИ ВІД ІОНІВ Fe^{2+}

Марта Пиріг, Зеновій Знак

Композит MnO_2/клиноптилоліт був синтезований шляхом розкладу $Mn(NO_3)_2$, розчином якого попередньо імпрегнували природний клиноптилоліт, під дією надвисокочастотного електромагнітного випромінювання (частота випромінювання 2,45 ГГц, потужність 200 Вт). На основі EDX-аналізу, встановлено, що допування клиноптилоліту відбувається як завдяки йонному обміну, так і адсорбції розчину $Mn(NO_3)_2$, а також визначено вміст мангану на поверхні та приповерхневих шарах частинок клиноптилоліту. Досліджено вплив pH і температури на швидкість окиснення йонів Fe^{2+} у модельних розчинах $FeSO_4$ з концентрацією Fe^{2+} 5±0.1 мг/дм^3 у колоні з використанням нативної форми клиноптилоліту та синтезованого композиту MnO_2/клиноптилоліт. Встановлено, що швидкість окиснення Fe^{2+} за присутності нативної форми клиноптилоліту за умов досліду дуже низька. Водночас, у разі використання композиту MnO_2/клиноптилоліт швидкість окиснення на один-два порядки більша. Встановлено, що найбільший вплив на перебіг окиснення йонів Fe^{2+} має значення pH середовища. За pH 8.5 і температури 20^{0}C час до повного окиснення йонів заліза(II) складає 70 с.

Ключові слова: клиноптилоліт, модифікування, частинки MnO_2, іони заліза(II), очищення води, окиснення.

RESEARCH ON THE EFFICIENCY OF THE MnO_2/CLINOPTILOLITE COMPOSITE SYNTHESIZED UNDER MICROWAVE RADIATION IN THE PROCESSES OF WATER PURIFICATION FROM Fe^{2+} IONS

Marta Pyrih, Zenovii Znak *

Lviv Polytechnic National University, Lviv, Ukraine

* **e-mail: zenovii.o.znak@lpnu.ua**

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