

KINETICS AND THERMODYNAMICS OF SILVER ION IMMOBILISATION BY NATURAL CLINOPTILOLITE

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ABSTRACT. Natural zeolites attract the attention as efficient supports of stable and monodispersed nanoparticles (NPs) for the preparation of various nanocomposites. The present work describes the results from the immobilisation of silver ions by purified natural zeolite - clinoptilolite, which is an initial step towards the production of nanocomposites "silver nanoparticles- zeolite". The effect of the concentration of silver ions in the form of AgNO₃ (within the range of 0.01÷0.10 M) and the ratio of the zeolite mass to the volume of AgNO₃ solution (ratio m:v being from 1:10 to 1:100) on the silver immobilisation has been investigated and the optimum conditions selected. The highest load of Ag⁺ ions by zeolite was achieved when one gram of zeolite contacted with 40 mL of 0.05 M AgNO₃ solution or with 20 mL of 0.10 M AgNO₃ solution (equivalent to 2 mmol Ag⁺ ions per 1 g zeolite). It was established that the kinetics of Ag⁺ ions immobilisation by natural zeolite can best be described by the pseudo-first order kinetic equation, whereas the thermodynamics - by the Freundlich adsorption isotherm.

Keywords: natural clinoptilolite, silver nanoparticle precursor, kinetics and thermodynamics of Ag⁺ immobilisation

КИНЕТИКА И ТЕРМОДИНАМИКА НА ИМОБИЛИЗАЦИЯ НА СРЕБЪРНИ ЙОНИ ОТ ЕСТЕСТВЕН КЛИНОПТИЛОЛИТ

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РЕЗЮМЕ. Естествените зеолити представляват ефективен носител на стабилни и монодисперсни наночастици (NPs) за получаване на нанокomпозитни материали. Настоящата работа описва резултатите от имобилизирането на сребърни йони върху пречистен естествен зеолит - клиноптилолит, което е начална стъпка от процеса на получаване на нанокomпозити "сребърни наночастици-зеолит". Изследвано е влиянието на концентрацията на сребърните йони (под формата на AgNO₃) в интервала 0.01÷0.10 M и на съотношението маса на зеолита към обем на разтвора от 1:10 до 1:100, върху степента на задържане на Ag⁺ йони. Намерено е, че оптималните условия за постигане на най-голямо натоварване на зеолита със Ag⁺ йони са един грам зеолит, контактуващ с 40 mL 0.05 M разтвор на AgNO₃ или с 20 mL 0.10 M разтвор на AgNO₃ (еквивалентни на 2 mmol Ag⁺ йони за 1 g зеолит). Установено е, че кинетиката на имобилизация на Ag⁺ йони от естествения зеолит най-добре се описва от кинетичното уравнение за псевдо-първи порядък, а термодинамиката - от адсорбционната изотерма на Фройдлих.

Ключови думи: естествен клиноптилолит, прекурсор на сребърни наночастици, кинетика и термодинамика на имобилизация на Ag⁺ йони

Introduction

The antimicrobial properties of silver ions and silver nanoparticles (AgNPs) have been well known for a long time. AgNPs and materials on their basis are an important means of disinfection of potable water (Rai et al., 2009).

Environmental applications of AgNPs require stable nanoparticles (NPs) that do not aggregate easily. The immobilisation of AgNPs on solid surfaces or their incorporation in a solid matrix provides stability and thus facilitates the reuse of NPs. The structure of natural zeolite consists of primary building units, i.e. the SiO₄ and AlO₄ tetrahedra. They are connected via oxygen ions into secondary building units which are then linked into a three-dimensional crystalline structure of zeolite. The substitution of Si by Al defines the negative charge of the zeolite framework which is compensated by alkaline and earth alkaline metal cations. Because of their negative charge on the surface, natural zeolites appear as cation exchangers (Margeta et al., 2013). Zeolites are mesoporous ion exchange materials with a stable network of hollow channels and pores within the size range of most monoatomic ions. Because of their thermal stability and unique interconnected porous microstructure, natural and

synthetic zeolites have been used as templating support materials to host a variety of metallic species including silver. Studies have shown that the porous internal network structure of zeolites provides an ideal and stable template for the formation and growth of particles with nanometre dimensions. Even more, nanoparticles are physically prevented from agglomeration to form larger nanoparticles or micron-sized particles as they are individually separated within the discrete pores and channels of the zeolite interior (Yee et al., 2015).

Zeolites have a strong affinity for Ag⁺ (Scacchetti et al., 2017). Silver ion-exchanged chabazite has shown the capability to precipitate silver nanoparticles at its surface after thermal reduction in air, Ar and H₂, with a size depending on the reduction environment (Liu et al., 2009).

It has been reported that the concentration and size of the formed AgNPs depend on the initial concentration of Ag-bearing solutions contacting with the zeolite and on the contact time (Guerra et al., 2012; Yee et al, 2015).

The present work aimed to explore the optimum conditions for the highest immobilisation degree of silver ions by purified natural zeolite - clinoptilolite, as an initial step to producing

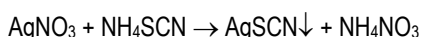
nanocomposite “silver nanoparticles–zeolite”. The impact of the ratio AgNO₃ solution volume to zeolite mass, as well as the influence of the initial concentration of the AgNO₃ solution that contacts with the zeolite on the silver ions uptake has been investigated. The results from this study could also be used when the aim is to adsorb Ag⁺ from silver-bearing wastewater.

Methods and materials

Natural zeolitic rock containing mainly clinoptilolite was used from the East Rhodopes region of Bulgaria. It was milled and the fraction of 0.09-0.325 mm was deployed. Zeolite was purified following a procedure described by Tomašević-Čanović (2005) and modified by us. Zeolite was washed with acidified water (pH=4.6, adjusted by HCl). In a typical procedure, 350 g of zeolite were placed 3 consecutive times (each one lasting for 24 hours) in contact with 700 mL of acidified water. Then, zeolite was washed by placing it in contact with 700 mL of distilled water for 2 hours at 60°C, 6 consecutive times, while it was stirred with a magnetic stirrer. The naturally adsorbed heavy metal ions were removed with a 0.05 M solution of EDTA by the treatment of zeolite for 2 hours at 60°C at the ratio of solid:liquid = 1:10. Then, zeolite was washed with distilled water again, as it is described above. In all washing steps, the contacted water was decanted off and then a new portion of water was poured into the beaker. Finally, zeolite was separated from the liquid by filtration, dried for 24 hours at 105°C, and supplied for analysis.

The chemical composition of zeolite was determined by means of the classical silicate analysis (in mass %): SiO₂ – 70.19, Al₂O₃ – 10.90, CaO – 2.87, MgO – 0.51, K₂O – 3.41, Na₂O – 0.36, Fe₂O₃ – 0.28, MnO – 0.04, TiO – 0.06, P₂O₃ < 0.05, SO₃ < 0.05, and LOI – 10.99. The theoretical cation exchange capacity (TCEC) of the natural zeolite (the sum of exchangeable cations such as Na⁺, K⁺, Ca²⁺ and Mg²⁺) was found to be 211 meq/100 g zeolite. It is of the same range as the TCEC determined by other authors for clinoptilolite from our region (Tomašević-Čanović, 2005; Margeta et al., 2013; Santiago et al, 2016). The X-ray diffraction (XRD) of purified zeolite reveals that it consists of 72.7% Clinoptilolite-Ca [Ca₃(Si₃₀Al₆)O₇₂·20H₂O] and 27.3% Barrerite [(Na,K,Ca_{0.5})₂(Al₂Si₇O₁₈)·7H₂O].

Solutions containing different concentrations of silver ions (Ag⁺) were prepared by dissolving AgNO₃ (p.a.) in distilled water. The accurate concentration of Ag⁺ ions was determined by titration with NH₄SCN solution in acidic medium in the presence of ammonium iron(III) sulfate, NH₄Fe(SO₄)₂·12H₂O (Korostelev, 1985). In the course of the analysis, the following reactions proceed:



The conditions for all performed experiments of Ag⁺ ion immobilisation by zeolite are given in Table 1.

Experiments were conducted batch-wise: a certain amount of zeolite was magnetically stirred in AgNO₃ solution with a

predetermined concentration (0.01 M, 0.025M, 0.05 M, 0.075M, and 0.10 M). The solution pH was adjusted to 6 by 1M HNO₃ to prevent the precipitation of silver ions (Charlot, 1969). Variations in the ratio between the mass of zeolite and the volume of AgNO₃ solution (denoted below as solid to liquid ratio, or m:v) were studied, namely 1:10, 1:20, 1:40, and 1:100. Aliquot portions of 10 mL were taken at particular time (2, 5, 10, 20, 30, 45, 60, 90, 120, 180, 240 min) and the amount of Ag⁺ ions remaining in the solution was determined by titration against NH₄SCN solution. Care was taken so that the total amount of the aliquots would be less than 10% of the whole volume of the solution contacting with zeolite. The process was monitored until the equilibrium was reached. Ag-loaded zeolite was collected by filtration and washed with distilled water till a negative reaction for Ag⁺ in the washings was observed. It was dried at 60°C for 8 h. During all experiments, precautions were taken due to silver light sensitivity. Each experimental result was obtained by averaging the data from duplicate samples.

Table 1. Experimental conditions of Ag⁺ ion immobilisation by zeolite

Experiment №	AgNO ₃ concentration (M)	Zeolite mass to volume of AgNO ₃ solution ratio (m:v)
1	0.05	1:10
2	0.05	1:20
3	0.05	1:40
4	0.05	1:100
5	0.01	1:20
6	0.025	1:20
7	0.075	1:20
8	0.10	1:20

Removal of Ag⁺ from the initial solution was calculated using the equation:

$$\text{Removal, \%} = [(C_0 - C_\tau) / C_0] \times 100 \quad (1)$$

where C₀ is the initial and C_τ is the concentration of Ag⁺ at particular time τ, mg/L. Kinetic data were fitted to the following kinetic equations:

For the first order irreversible reactions:

$$\ln (C_0 / C_\tau) = k \times \tau \quad (2)$$

For the second order irreversible reactions:

$$(C_0 - C_\tau) / (C_0 \cdot C_\tau) = k \times \tau \quad (3)$$

For the Lagergen pseudo-first order reactions:

$$\ln (q_e - q_\tau) = \ln q_e - k_{\text{ads}} \times \tau \quad (4)$$

where k is the reaction rate constant; C₀, C_τ and τ are as described above; q_e (mg Ag⁺/g zeolite) is the amount of solute adsorbed at the equilibrium; q_τ (mg/g zeolite) is the amount of solute adsorbed at time τ; k_{ads}, min⁻¹ is the adsorption rate constant. The slope of the linear plot of ln (q_e – q_τ) against τ gives k_{ads}.

Langmuir and Freundlich isotherm models were studied for their ability to describe the equilibrium sorption distribution.

The Langmuir isotherm:

$$q_e = (Q_{max} \times K_L \times C_e) / (1 + K_L \times C_e) \quad (6)$$

The Freundlich isotherm:

$$q_e = K_F \times C_e^n \quad (7)$$

where q_e is metal concentration on the zeolite at equilibrium (meq of metal ion/g of zeolite), C_e is the equilibrium metal concentration in the aqueous phase (mg/L), Q_{max} is the maximum achievable capacity (meq/g), K_L (L/mg) is the Langmuir constant, n is the Freundlich intensity parameter, and K_F is the Freundlich isotherm constant (mg/g). If the plot of C_e/q_e as a function of C_e is a straight line, the adsorption process can be described by the Langmuir isotherm. If the plot $\log q_e$ vs $\log C_e$ is a straight line, the adsorption process is best described by the Freundlich isotherm.

Results and discussion

The kinetics of Ag^+ uptake at an initial concentration of 0.05 M $AgNO_3$ and at different ratios of solid to liquid is presented in Fig. 1. The kinetics of Ag^+ uptake at the ratio of solid to liquid 1:20 and at different initial concentrations is presented in Fig. 2.

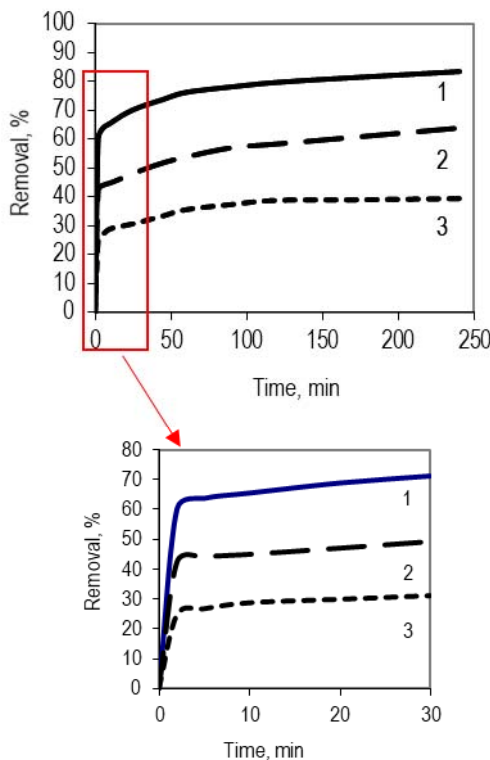


Fig. 1. Kinetics of Ag^+ uptake at an initial concentration of 0.05 M $AgNO_3$: — $m:v = 1:10$ (1), - - - $m:v = 1:20$ (2), - - - - $m:v = 1:40$ (3)

The kinetic curves reveal that the reaction consists of two stages, “fast” and “very slow”, at all studied $m:v$ ratios and initial concentrations of Ag^+ . Practically, the process reaches

equilibrium in about 2 hours. The relatively short ion exchange time of 2 hours has been found as sufficient to produce optimum Ag^+ uptake into the zeolite pores by other authors as well (Jiraroj et al., 2014; Yee et al., 2015).

It has been found that in all experiments, the kinetics of Ag^+ immobilisation by zeolite is best described by the pseudo-first order kinetic equation. The coefficients of determination R^2 are close to unity as presented in Table 2. Generally, this equation describes an adsorption reaction at the liquid/solid interface where a steep rise of the uptake at short times is observed (fast initial step). In such case, in calculation of the reaction rate, the data close to or at equilibrium are not included since a methodological bias is introduced (Simonin, 2016). That is why the reaction rate constants (k_{ads}) presented in Table 2 are calculated by taking into account the data for the first 90 minutes of the reaction.

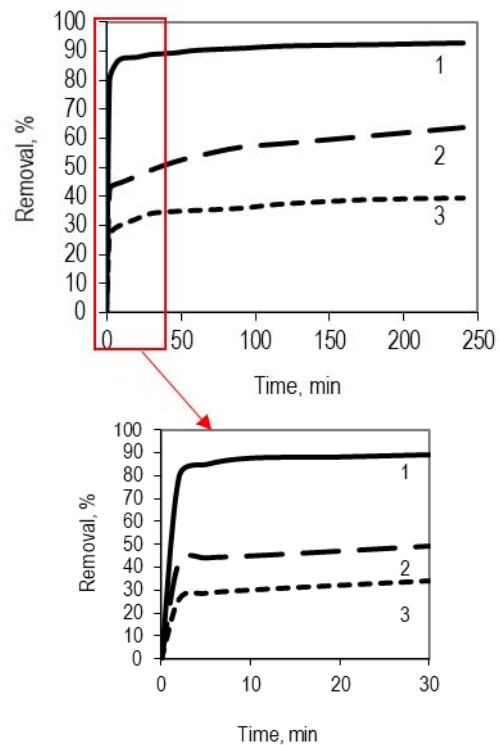


Fig. 2. Kinetics of Ag^+ uptake at the ratio of solid to liquid 1:20 and at initial concentrations of $AgNO_3$: — 0.01 M (1) - - 0.05 M (2) - - - 0.10 M (3)

Table 2. R^2 values for fitting the experimental data to pseudo-first order kinetic equation and reaction rate constant

Experiment Ne	1	2	3	5	8
R^2	0.985	0.982	0.961	0.951	0.971
k_{ads}, min^{-1}	0.0156	0.0146	0.0224	0.0235	0.0172

The maximum uptake values of Ag^+ ions by zeolite for all samples, calculated by using the removed amount of Ag^+ from the solution at 240 min (when equilibrium was achieved), are presented in Table 3.

The amount of Ag⁺ immobilised by zeolite is in the range of approximately 20-80 mg per gram zeolite (Table 3). Our findings are in line with the results of Akhigbe and coauthors (Akhigbe et al., 2016) who found the loading of 43.4 mg Ag⁺/g zeolite when the process was carried out on natural British clinoptilolite at m:v =1:2.5, initial AgNO₃ concentration of 3% (w/v), and reaction time of 24 hours.

Table 3.
Maximum uptake of Ag⁺ ions by zeolite

Experiment №	1	2	3	4	5	6	7	8
mgAg ⁺ /g zeolite	40.4	60.3	76.8	39.7	19.0	32.2	68.0	78.2

Data presented in Tables 2 and 3 show that both factors solid to liquid ratio and the initial concentration of silver ions in the solution influence the maximum loading on zeolite.

At an initial concentration of 0.05 M AgNO₃ (experiments 1 - 4, Table 1), the amount of immobilised Ag⁺ ions increases with the increase of the ratio m:v up to 1:40, while a further increase of the volume of Ag⁺ solution gives lower loading (Table 3). The reduced immobilisation could be due to the insufficiency of adsorption sites on zeolite capable to "bind" the large number of Ag⁺ present in the solution.

If the ratio solid to liquid is kept constant (m:v=1:20, experiments 5-8, Table 1), then the increase of Ag⁺ concentration causes a gradual increase of Ag⁺ loading and the greatest amount of Ag⁺ held on zeolite is 78.2 mg/g (Table 3). It was reported by Yee and coauthors (2015) that the use of a higher concentration of the AgNO₃ (up to 1.0 M, m:v=1:20) led to a greater concentration of Ag⁺ ions immobilised on zeolite ZSM-5 and, thus, a higher concentration of AgNPs was achieved.

The highest rate constant (0.0235 min⁻¹) was determined for experiment 5 where the ratio m:v = 1:20 and the concentration of AgNO₃ was the lowest (0.01 M, Table 2). At the same time, the amount of the immobilised Ag⁺ per gram of zeolite was the lowest one (19.0 mg/g, Table 3). In such case, almost all available Ag⁺ ions were immobilised, but because their initial concentration in the solution was low, the resulted loading was low. Although a similar value of the rate constant (0.0224 min⁻¹) was found for experiment 3 (0.05 M, m:v=1:40), the Ag⁺ uptake (76.8 mg/g) was significantly higher compared to experiment 5 due to a fivefold higher concentration of initial solution in experiment 3 (Table 3).

As can be seen in Table 3, very close values were obtained for the Ag⁺ loading (76.8 mg/g and 78.2 mg/g for experiment 3 and experiment 8, respectively), though a twice concentrated solution in experiment 8 was used (0.10 M and m:v=1:20). Obviously, the difference between experiments 3 and 8 is within the experimental uncertainties. Thus, one can propose that 76-78 mg/g is the optimum Ag⁺ loading on zeolite ensured by the contact of 1-gram zeolite with 40 mL of 0.05 M AgNO₃ solution or 20 mL of 0.10 M AgNO₃ solution (equivalent to 2 mmol Ag⁺ ions).

This amount seems to be the optimum one with respect to the capacity of zeolite to be loaded with Ag⁺. Zeolite prepared

under those conditions is worth undergoing further chemical reduction or calcination for obtaining AgNPs.

Experimental data fitting the isotherm equations have shown that the process is best described by the Freundlich isotherm with R²=0.983. The values for the Freundlich intensity parameter and the Freundlich isotherm constant are graphically found and are, respectively, n=0.65 and K_F=395 mg Ag⁺/g zeolite. The adsorption intensity n is less than 1 and, therefore, indicates a favourable sorption of Ag⁺ on the zeolite.

Conclusions

As a result of the experiments carried out on Ag⁺ immobilisation by natural zeolite, the following conclusions can be drawn:

1. The kinetics of Ag⁺ immobilisation by natural zeolite consisting mainly of clinoptilolite is best described by the pseudo-first order kinetic equation.
2. The uptake of Ag⁺ by the natural zeolite in the studied AgNO₃ concentration range of 0.01-0.10 M is best described by the Freundlich adsorption isotherm with constants n=0.65 (showing the favourable sorption) and K_F=395 mg Ag⁺/g zeolite, respectively.
3. Within the studied AgNO₃ concentration range of 0.01-0.10 M and the ratio of solid to liquid in the range of 1:10-1:100, the optimum conditions for achieving the highest Ag⁺ loading by zeolite are one gram of the zeolite contacting with 40 mL of 0.05 M solution or with 20 mL of 0.10 M solution.
4. In our future work, the prepared silver-loaded zeolite can be used as a precursor for the synthesis of AgNPs supported on zeolite.

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