

Iodide Removal by Use of Ag-Modified Natural Zeolites

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Abstract. In the present work Ukrainian clinoptilolite was modified with Ag and applied for the removal of iodide from aqueous solutions. The effect of three different modifications was studied, one resulting in an Ag⁺ ion exchanged form, and two resulting in zeolites decorated with silver oxide and zero valent metallic nanoparticles. The results indicated the strong potential affinity of the Ag-modified zeolite materials towards iodide.

1. Introduction

Iodine is an essential element that's necessary for a normal thyroid function. However, high concentration of iodine in food and water calls a great concern of production of the congenital goiter. It should be pronounced that little attention has been paid to the role of iodine chemical form in its toxicity [1]. Authors [2] demonstrated that iodide has significant influence on the thyroid weight in male rats, although the iodide has low effect on the thyroid gland weight it changes thyroid hormones production level in both sexes, known as Wolff-Chaikoff effect [3]. WHO reports [4] an excessive iodine consumption related to numerous factors such as high level of table salt iodization or consuming iodine-rich food. Asian diet contain iodine-rich food [5], whereas in Europe drinking water with high level of iodine have been reported [6]. Combination of high iodine concentration in diet and drinking water with iodine supplementation leads to chronic iodide exposure resulting in iodism [7]. Iodine/iodide excess is a recognisable environmental risk factor for development of thyroid disorders and population of elderly, pregnant, fetuses and neonates are more susceptible to excess iodine induced diseases. Another concern with iodide/iodine is related to radioactive isotopes released from nuclear power plants. In the Fukushima Daiichi Nuclear Plant accident (Japan, 2011), a large amount iodine radioisotope was released into the environment [8]. Therefore novel adsorbents towards to iodine/iodide removal should be developed in order to reduce their concentration in drinking water. The use of zeolites (aluminosilicate porous natural materials) as adsorbents has attracted considerable attention due to their structural and chemical properties. Clinoptilolites have been found in many geological areas around the world and widely used in various applications [9]. A natural Ukrainian zeolite-Sokyrnit (NZU) is the mineral of volcano origin deposit in Transcarpathian region of Ukraine [10], which chemical composition is (Na, K)₄CaAl₆Si₃₀O₇₂·24H₂O [11]. Transcarpathian zeolites have been successfully applied in the environmental protection chemistry and industry [12]. Their non-toxic and non-swelling properties, thermal stability and potential of regeneration as well as high rate of ion exchange makes them excellent candidates in sorption processes. Clinoptilolites have been widely used in adsorption of cationic species due to negatively charged surface and presence of exchangeable cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) [13], however they show a poor affinity towards anions [14]. Surfactants and noble metal species can be used to enhance clinoptilolite affinity towards to iodide [15, 16]. I⁻ anions are readily react with silver oxide (Ag₂O) to form the water-insoluble



silver iodide [17]. Therefore, the aim of this study is to tailor the surface properties of NZU for iodide removal. The modification procedures were based on the use of AgNO₃ impregnation followed by thermal treatment and redox reaction with sodium borohydride in case of AgNPs formation. Preliminary adsorption study was carried out for water deiodification with modified and pristine NZU.

2. Materials and Methods

2.1. Materials

To study iodide adsorption NZU of particle size of 2-5 mm was supplied by the TM “Transcarpathian zeolitic factory” (Khust district, Ukraine). Chemical reagents such as NaCl (≥99.0%), KI (≥99.0%), AgNO₃ (>99.9%) and NaBH₄ (99.0%) (all from Sigma-Aldrich) were used as received. Ultrapure water with resistivity of 18.3 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Millipore).

2.2. Ion exchanged zeolites

The zeolite batch was firstly dried at 150 °C under for 24 h to remove the material humidity. The powder sample was sieved in a vibratory sieve shaker AS200 (Retsch), samples with particle diameters ranging from 0.8 to 1.6 mm were collected and used for ion exchange with NaCl. Homo-ionic Na-NZU was obtained via impregnation zeolite with 1 M NaCl for at 60 °C in regards to the procedure described elsewhere [18]. Obtained homo-ionic clinoptilolite (NZU_Na) was washed with DI water in order to remove the occluded NaCl, filtered, dried at 60 °C and stored in desiccator for the further usage. Ag⁺ substituted zeolite was prepared from NZU_Na via impregnation with 0.04 M AgNO₃ in a light-shielded conditions [19]. In typical procedure 100 g of NZU_Na was impregnated with 250 ml of 0.04 M AgNO₃ at ambient temperature for 24 h, and then obtained zeolite (NZU_Ag⁺) was filtered and dried in the bench oven for 8h at 60 °C.

2.3. Silver oxide-impregnated zeolites

Deposition of Ag₂O over the NZU_Na surface was performed as described in [20]: 3 g of NZU_Na was dispersed into the AgNO₃ solution (0.1 M, 0.2 L) under continuous agitation for 48 h. Sample then was filtered and dried in the bench oven for 24h at 60 °C and labeled as NZU_Ag₂O.

2.4. Silver metal nanoparticles-impregnated zeolites

The three-steps procedure for Ag nanoparticle synthesis on the surface of NZU was derived from [20]. Prior to the modification NZU_Na was calcinated at 300 °C for 3h. First two stages of synthesis were performed via subsequent saturation with 10 mM AgNO₃, in light-shield condition at ambient temperature for 8h, followed by drying at 180 °C for 6h. To reduce the Ag₂O formed on the NZU surface the borohydride reduction method was adapted from [21]; for each batch of Ag₂O impregnated NZU (10 g) 20.0 mL of 50 mM NaBH₄ was used. The mixture was stirred in the dark for 8 h to the reaction completion; afterwards sample was rinsed to remove unreacted salt until pH neutral, filtered and dried in a bench oven at 90 °C for 8 h and stirred in desiccator prior to the use.

2.5. Iodine adsorption

All solutions were prepared using ultra-pure water. Briefly, iodide solution was prepared by dilution of 1000 mg L⁻¹ I stock solution (KI). Batch experiments of iodide adsorption were carried out by immersion of zeolite samples equivalent to 0.1 g dry weight with 10mL of potassium iodide (100 ppm) solution. This was performed in PP centrifuge tubes fitted with caps, at 25 °C for 24 h [22]. Then, the supernatant solution was separated from the mixture solution by filtration with 0.22 μm MF membrane. The concentration of I⁻ ions remaining in solution was determined by ion chromatography (Model 930 Compact IC Flex, Metrohm, Switzerland). The amount of I⁻ ions adsorbed by zeolite q_t (mg/g) is calculated using the following Eq. (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where C_0 and C_t are the initial and a time t liquid-phase I concentrations (mg L^{-1}), V is the volume of the solution (mL), and m is the mass of dry sample used (g).

2.6. Characterization of materials

The specific surface area properties of the natural and modified NZU were determined using an Autosorb 1C (Quantachrome Instruments). Chemical composition of pristine and modified samples was determined using X-ray fluorescence (XRF) spectroscopy using a PANalytical Axios mAX instrument and samples were prepared in an automatic fusion system (XrFuse 6, XRF Scientific, Brussels, Belgium). The adsorption isotherms of N_2 were determined at the temperature of the liquid nitrogen. Prior to its analysis, the samples were degasified for 24 h at 120°C . Wide-angle X-ray diffraction (XRD) was used to characterize the zeolite diffraction patterns. All measurements were collected over the 2θ range from 10° to 90° on a Rigaku SmartLab diffractometer equipped with a $\text{CuK}\alpha$ radiation source (0.1549 nm). Ion chromatograph (930 Compact IC Flex) was used to analyse iodine concentration.

3. Results and Discussion

The nitrogen adsorption-desorption isotherm (not shown here) are classified as isotherms of IV Type and the BET surface area (Table 1) of raw NZU is small ($12.6 \text{ m}^2/\text{g}$). Based on the nitrogen adsorption-desorption study (and confirmed with XRD) it can be stated that the clinoptilolite skeleton does not change with modification procedure, but average pore size changes as result of cation exchange (decrease) and sodium borohydride treatment (increased).

Table 1. Porosimetry analysis of natural and modified zeolites.

| Samples | Porosimetry data | | |
|----------------------------|---|------------------------------|------------|
| | S_{sp} (m^2/g) | V (cc/g) | D_p (nm) |
| NZU | 12.6 | 0.027 | 5.8 |
| NZU_ Na^+ | 15.0 | 0.032 | 2.98 |
| NZU_ Ag^+ | 14.9 | 0.076 | 3.15 |
| NZU_ Ag_2O | 8.7 | 0.061 | 5.4 |
| NZU_ AgNPs | 11.2 | 0.071 | 11.0 |

Mineralogical composition of each sample was determined by XRD analysis (Figure 1). Natural zeolite is primary comprised of clinoptilolite, while XRD spectra of modified samples contained peaks of silver corresponding to the formation of Ag-forms of clinoptilolite and heulandite (Table 2).

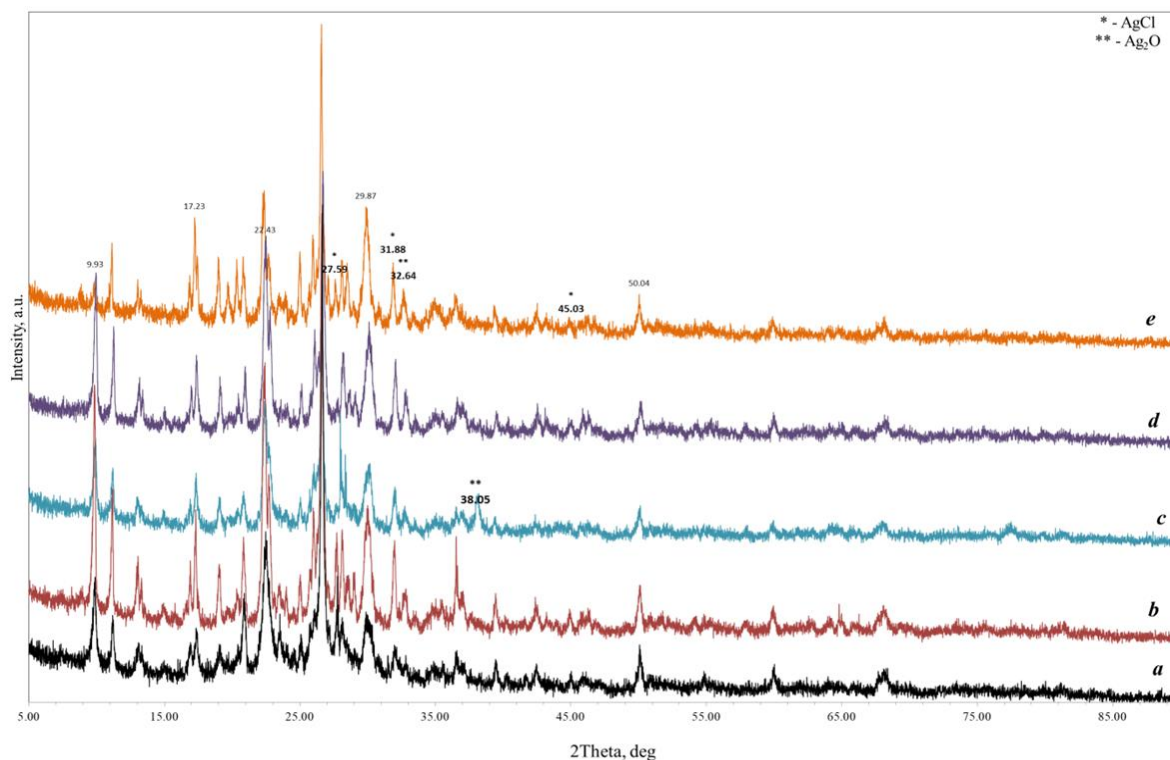


Figure 1. XRD patterns of NZU (a), NZU_{Na} (b), NZU_{AgNPs}(c), NZU_{Ag⁺}(d) and NZU_{Ag₂O} (e).

XRD spectra of NZU- Ag_2O (Figure 1, e) shows bands of silver at 27.59, 31.88 and 45.03 $2\theta^\circ$ (ref. file 01-075-9577, Chlorargyrite). The peak at 38.05 2θ in spectra of NZU_{AgNPs} (Figure 1, c) is characteristic of Ag metal (JCPDS, File No. 4-0783), which confirms the formation of Ag nanoparticles on the surface of zeolite.

Table 2. XRD analysis of zeolites.

| Samples | Crystalline structure | |
|--------------------------------|-----------------------|-----------------|
| | Compound name | JCPDS, File No. |
| NZU | Clinoptilolite | 01-079-1461 |
| NZU _{Na⁺} | Clinoptilolite-Na | 01-079-1461 |
| NZU _{Ag⁺} | Clinoptilolite-Ag | 01-081-8531 |
| NZU _{Ag₂O} | Clinoptilolite-Ag | 01-081-8531 |
| NZU _{AgNPs} | Heulandite (Ag) | 01-084-0419 |

According to the iodine adsorption experiments, zeolite samples which are non-loaded with silver had statistically insignificant adsorption values (Table 3, samples NZU and NZU_{Na⁺}). The values of I adsorption extraction rate (Table 3) increased with the increase in silver content in composite, however this increase is non-monotonic and an influence of silver loading, particle size and chemical composition on the iodine extraction should be investigated further.

Table 3. Iodine adsorption results.

| Sample | Ag content* (wt%) | Iodine extraction rate (%) |
|--------------------------------|-------------------|----------------------------|
| NZU | 0.0 | 0.53 |
| NZU _{Na⁺} | 0.0 | 0.72 |
| NZU _{Ag⁺} | 0.91 | 67.0 (± 0.3) |
| NZU _{Ag₂O} | 7.9 | 100.0 (± 0.5) |

| | | |
|-----------|-----|--------------------|
| NZU_AgNPs | 2.2 | 79.0 (± 0.4) |
|-----------|-----|--------------------|

* - determined by X-ray fluorescence (XRF).

4. Conclusions

This study demonstrates facile and low-tech method of natural Ukrainian clinoptilolite surface modification with AgNO₃. A subsequent physical-chemical treatment of Ag⁺ impregnated zeolites leads to formation silver species (Ag₂O and AgNPs). Zeolite modification was confirmed by XRD analyses, without observing significant changes in zeolite skeleton; nevertheless, reducing of silver species on the zeolite surface with sodium borohydride leads to doubling in pore diameters. The adsorption properties of pristine and modified zeolites in aqueous solution towards iodide anion were studied and sample NZU_Ag₂O gave the best results. Ag-modified forms of clinoptilolite are promising materials for iodine removal from aqueous solution. Implementation of such synthetic approach paves the way for further research on the mechanism of anionic extraction.

5. References

- [1] Medeiros - Neto, G.A., et al., *Congenital goitre and hypothyroidism with impaired iodide organification and high thyroid peroxidase concentration*. Clinical Endocrinology, 1979. 11(2): p. 123-139.
- [2] Sherer, T.T., K.D. Thrall, and R.J. Bull, *Comparison of toxicity induced by iodine and iodide in male and female rats*. Journal of Toxicology and Environmental Health, 1991. 32(1): p. 89-101.
- [3] Eng, P.H.K., et al., *Escape from the Acute Wolff-Chaikoff Effect Is Associated with a Decrease in Thyroid Sodium/Iodide Symporter Messenger Ribonucleic Acid and Protein**. Endocrinology, 1999. 140(8): p. 3404-3410.
- [4] Zimmermann, M., *Iodine Deficiency and Excess in Children: Worldwide Status in 2013*. Endocrine Practice, 2013. 19(5): p. 839-846.
- [5] Teas, J., et al., *Variability of Iodine Content in Common Commercially Available Edible Seaweeds*. Thyroid, 2004. 14(10): p. 836-841.
- [6] Andersen, S., S.B. Petersen, and P. Laurberg, *Iodine in drinking water in Denmark is bound in humic substances*. European Journal of Endocrinology, 2002. 147(5): p. 663-670.
- [7] Rivero, J.D., C. Cochran, and F.S. Celi, *Acute iododerma: An uncommon serious adverse event associated with saturated solution of potassium iodide treatment*. AACE Clinical Case Reports, 2018. 4(2): p. e127-e130.
- [8] Xu, S., et al., *Iodine Isotopes in Precipitation: Temporal Responses to I¹²⁹I Emissions from the Fukushima Nuclear Accident*. Environmental Science & Technology, 2013. 47(19): p. 10851-10859.
- [9] Stocker, K., et al., *Characterization and Utilization of Natural Zeolites in Technical Applications*. BHM Berg- und Hüttenmännische Monatshefte, 2017. 162(4): p. 142-147.
- [10] Moklyachuk, L., et al., *The use of natural zeolites impregnated with zinc and copper ammoniates as carriers of micronutrients in growing vegetables*. Emirates Journal of Food and Agriculture, 2013. 25(12): p. 980-985.
- [11] Tarasevich, Y.I., et al., *Physical and Chemical Properties of the Transcarpathian zeolite and its application as a filter material in water treatment*. Chem. Tech. Water, 1979. 1(1): p. 66-69.
- [12] Vasylechko, V.O., et al., *Adsorption of Copper on Transcarpathian Clinoptilolite*. Adsorption Science & Technology, 1999. 17(2): p. 125-134.
- [13] Delkash, M., B. Ebrazi Bakhshayesh, and H. Kazemian, *Using zeolitic adsorbents to cleanup special wastewater streams: A review*. Microporous and Mesoporous Materials, 2015. 214: p. 224-241.
- [14] Loganathan, P., et al., *Defluoridation of drinking water using adsorption processes*. Journal of Hazardous Materials, 2013. 248-249: p. 1-19.
- [15] Chebbi, M., et al., *Influence of structural, textural and chemical parameters of silver zeolites on the retention of methyl iodide*. Microporous and Mesoporous Materials, 2017. 244: p. 137-150.

- [16] Yu, F., et al., *Enhanced removal of iodide from aqueous solution by ozonation and subsequent adsorption on Ag-Ag₂O modified on Carbon Spheres*. Applied Surface Science, 2018. 427: p. 753-762.
- [17] Wiberg, E., N. Wiberg, and A.F. Holleman, *Holleman-Wiberg's Inorganic Chemistry*. 1st ed. 2001, New York: Academic Press. 1884.
- [18] Lihareva, N., et al., *Ag⁺ sorption on natural and Na-exchanged clinoptilolite from Eastern Rhodopes, Bulgaria*. Microporous and Mesoporous Materials, 2010. 130(1): p. 32-37.
- [19] Akhigbe, L., S. Ouki, and D. Saroj, *Disinfection and removal performance for Escherichia coli and heavy metals by silver-modified zeolite in a fixed bed column*. Chemical Engineering Journal, 2016. 295: p. 92-98.
- [20] Bo, A., et al., *Removal of radioactive iodine from water using Ag₂O grafted titanate nanolamina as efficient adsorbent*. Journal of Hazardous Materials, 2013. 246-247: p. 199-205.
- [21] Mulfinger, L., et al., *Synthesis and Study of Silver Nanoparticles*. Journal of Chemical Education, 2007. 84(2): p. 322.
- [22] Yoshida, S., Y. Muramatsu, and S. Uchida, *Studies on the sorption of I⁻ (iodide) and IO₃⁻ (iodate) onto Andosols*. Water, Air, and Soil Pollution, 1992. 63(3): p. 321-329.

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