

## PRELIMINARY ASSESSMENT OF MODIFIED KAZAKH NATURAL ZEOLITES AS POSSIBLE SORBENTS FOR $\text{MnO}_4^-$ REMOVAL FROM AQUEOUS SOLUTIONS

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**ABSTRACT.** A natural zeolite of Kazakh origin, as well as its three different types of chemically modified versions, were assessed from the point of view of permanganate removal yield from aqueous solutions. Modification was carried out by means of di-dodecyl-dimethyl-ammonium bromide surfactant treatment type (1). Types (2) and (3) were treated prior to DDAB with HCl or NaCl, respectively. All sorbents display broad ranges of particle size distribution. Modification of the natural form enhances the specific surface as well as the pore volume, yet influences not in the same way the sorption yield. The process is slow, however, short- and long-term effectiveness are affected by preparation procedures. The most promising yield is exhibited by the natural zeolite that was subject to a combined acid - surfactant treatment.

**Keywords:** *Kazakh zeolite, chemical surface modification, permanganate adsorption*

### INTRODUCTION

Wastewater pollution by heavy metal ions is an important issue for many industrial enterprises. Improperly treated wastewater can reach natural reservoirs, where heavy metals may accumulate as bottom sediments, precipitate as carbonates or sulfates and become hence a secondary pollution source [1,2]. Removal of such pollutants is therefore a necessity.

Within this context, sorption on solid sorbents is nowadays one of the most common ways of wastewater treatment, with results and efficacy depending on physico-chemical features of both adsorbents and adsorbates [2].

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Natural silicate materials have several properties that recommend them as sources for sorbents, catalysts, plasticizers, reinforcing additives, etc. [1]. Their main advantages are availability and relatively low price as compared to synthetic materials. One of the most effective type of sorbents are zeolites, hydrated aluminosilicates with cage-like structures ( $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons [2]), an available surface of up to  $100 \text{ m}^2/\text{g}$ , and a high cation-exchange capacity. Crystals have a regular system of cavities that are interconnected by channels. Cations and water molecules are positioned in the channels, whereas cations are mobile and may be exchanged. They compensate the excess negative charge of the anionic part of the zeolite's framework. Due to the "channel-cavity" structure, these adsorbents have a well-developed inner surface that might be available for adsorbate molecules. There are around 50 types of natural and more than 150 types of synthetic zeolites used in different applications at the moment [2]. The most common type of natural zeolite is clinoptilolite.

To increase their sorption activity, zeolites may be chemically modified by a variety of different methods, such as: ion-exchange, changing of Si/Al ratio by direct synthesis in different conditions, de-cationization leading to hydrogen enriched zeolites, de-alumination by acid treatment, etc. The simplest way of modifying is by means of ion-exchange [3-6].

The ways of obtaining zeolite based sorbents that are modified by compounds which contain different functional groups, are widely studied recently. These functional groups act as additive active centers on the sorbent's surface. Examples of such modifiers are polymers, surfactants, acids, bases, etc. [7].

The permanent negative surface charge, which occurs as a result of long-lasting isomorphic replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the crystal framework tetrahedrons, permits the use of zeolites for effective adsorption of metal cations ( $\text{Mn}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{La}^{3+}$ ) and cationic dyes. On the other hand, as such, anions adsorb difficultly [2,8,9].

To improve the adsorption capacity of zeolites towards specific hydrophobic adsorbates, amphiphilic sorbents were developed by adsorption of cationic surfactants onto the external surface of zeolites [9]. Hence, the surfactant-modified zeolite becomes a so-called "organo-zeolite". Cationic surfactants are amphiphilic molecules which often contain a positively charged hydrophilic head (normally quaternary ammonium with a counter ion such as  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{SO}_3^{2-}$ ) and a relatively long hydrophobic tail (8 to 24 carbon atoms) [10-13]. It has been proved that the longer the hydrophobic chain, the more stable the retention of surfactant on the zeolite's surface.

Above the critical micelle concentration (CMC), the surfactant forms a bilayer / multilayer on the zeolite's surface [3-6]. The amount of retained surfactant depends primarily on its concentration. At low concentrations, the

surfactant cations will attach to the external surface of the zeolite through an ion-exchange mechanism, till the formation of a monolayer is completed. At higher concentrations, the second layer of surfactant may attach to the first one, due to hydrophobic interactions between the alkyl chains. The positively charged groups of the second layer will be oriented towards the bulk of the aqueous solution due to electrostatic repulsive forces of head groups between internal and external layers [1]. The formation of the second layer causes an excessive positive charge (close to the surface of the adsorbent), that further enables the adsorption of anions. Thereby, surfactant-modified zeolites are considered effective towards organic anions, especially to phenol and its by-products [14-16].

The purpose of this work was to assess the possibility of using surfactant-modified organo-zeolites of natural Kazakh source for efficient heavy metal anion removal from water. Permanganate was chosen as model anion, since its concentration in aqueous solutions is easily accessible by means of photometry. Effectiveness in sorption processes of different treatment methods of the natural zeolite was also assessed, *via* a removal yield, and compared to the performance of untreated zeolite. As such, this paper is a preliminary study. If positive conclusions are drawn, the Shankanai zeolite deposit of the Almaty region, in the Republic of Kazakhstan, may develop to a reliable local source for low-cost pollutant sorbents, especially since exceeding of permissible concentrations is reported for the majority of Kazakh water reservoirs [17], for both organic pollutants and some heavy metal ions (either cations or anions).

## RESULTS AND DISCUSSION

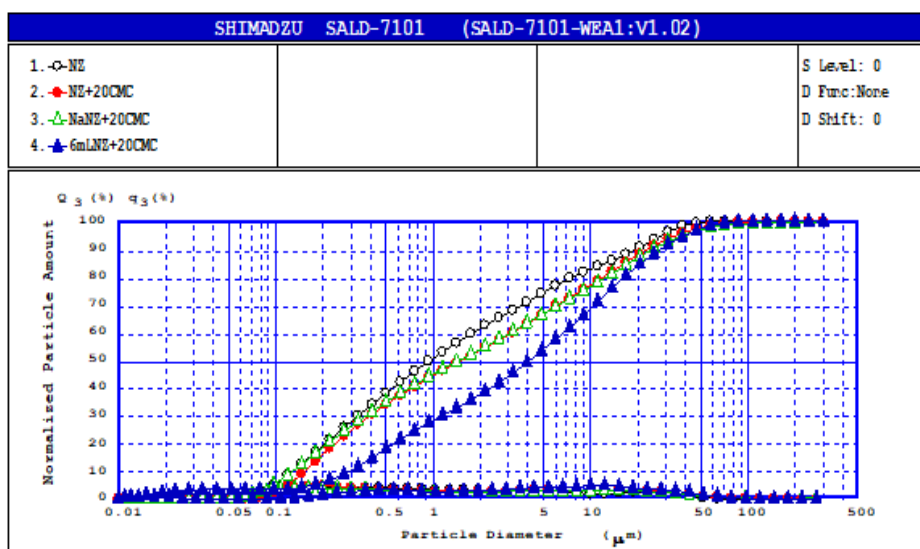
The employed zeolite comes from the Shankanai deposit, Almaty region, Republic of Kazakhstan. It belongs to the clinoptilolite type, related to the heulandite group. It is characterized by 3-dimensional aluminosilicate frameworks that mainly consist of 4-4-1-1 structural unit layers [16].

Three different types of natural zeolite (NZ) based, yet modified sorbents, were prepared (see detailed description of preparation in the experimental part). Type (1) refers to surface modified NZ by means of di-dodecyl-dimethyl-ammonium bromide (DDAB), a two-chained cationic surfactant. The main feature giving information about the shape and geometry of it, is its packing parameter of 0.620 [2]. Therefore, DDAB is expected to form on the surface of the absorbent flat structures (either lamellae or vesicle), when present in concentrations above the critical micelle concentration (CMC) [18] (1 CMC stands for 0.1 mM). Type (2) and (3) refer to sorbents that were treated

prior to DDAB surface modification, with hydrochloric acid or with sodium chloride, respectively. This kind of treatment was reported [6] to aid a more structured arrangement of surfactant molecules within the first layers on the sorbent's surface.

## Sorbent characteristics

Both natural zeolite and modified NZ are fine powders of brownish color. Results of particle size and distribution analysis for all main types of sorbents are presented in Figure 1.



**Fig. 1.** Distinctive and integrated particle size distribution curves of various sorbents. Black circles – NZ; Red circles – type (1) modified NZ; Blue triangles – type (2) modified NZ; Green triangles – type (3) modified NZ.

Figure 1 shows that particle size varies with an almost uniform distribution in a wide variety of values, over 4 orders of magnitude, from 0.01 to 100  $\mu\text{m}$ . Results are similar, regardless of the treatment to which NZ was subjected to. Such a broad range of particle size distribution is probably due to the manual dispersing of zeolite, without the employment of other grinding methods or granulometric fraction separation.

The values of specific surface and pore volume of both NZ and modified NZ sorbents, calculated according to the BET theory, are presented in table 1. It is obvious that DDAB surfactant treatment - type (1), and moreover, the prior acid to DDAB treatment - type (2), enhance both presented parameters. Type (3) treatment does not bring about an improvement, as compared to type (2).

Type (2) modified NZ shows best results. This is probably due to the enhancement of positive charges and/or ion-exchange on the zeolite's surface, carried out more effectively by the smaller sized  $H^+$  than by the larger  $Na^+$ . The result is a better and more structured coverage by DDAB, thus a favorable charged "head" and "tail" orientation for anion retention from the bulk solution.

However, the type (2) modified NZ prepared at different surfactant concentrations demonstrates that 4 times lower DDAB concentrations bring about a 50% increase of both specific surface and pore volume. This may be due to DDAB forming more dense lamellar layers at higher concentrations, and therefore block (fill in) some pores of the solid.

**Table 1.** Values of specific surface and pore size for unmodified and modified NZ. (Coding of samples is described in the Experimental section).

Type of sorbent	Specific	
	Surface (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
<b>Unmodified zeolite</b>		
NZ	4,53	0,002
<b>Modified Zeolite at same CMC of surfactant and different types of treatment</b>		
<b>Type (1): NZ+20CMC-DDAB</b>	8,26	0,004
<b>Type (2): NZ+HCl+20CMC-DDAB</b>	21,49	0,009
<b>Type (3): NZ+NaCl+20CMC-DDAB</b>	7,31	0,003
<b>Modified Zeolite of type (2) with different CMC of surfactant</b>		
<b>Type (2): NZ+HCl+20CMC-DDAB</b>	21,49	0,009
<b>Type (2): NZ+HCl+10CMC-DDAB</b>	29,21	0,013
<b>Type (2): NZ+HCl+5CMC-DDAB</b>	31,49	0,013

### Sorption experiments and assessment of sorption performance

These experiments were carried out by using the same volume of aqueous permanganate solution of initial 10 mg/L concentration. Identical amounts of all types of sorbents were added to it, in order to assess their sorption performance.

At predetermined time intervals (3, 24 and 72 hours respectively), the residual concentration **C** of  $\text{MnO}_4^-$  in the liquid phase (expressed in mg/L) was determined photometrically at 525 nm, by using the Lambert-Beer calibration in equation (1) - where A stands for absorbance.

$$A = 0.005 + 0.078 \mathbf{C} \quad (R^2 = 0.998 / 7 \text{ points}) \quad (1)$$

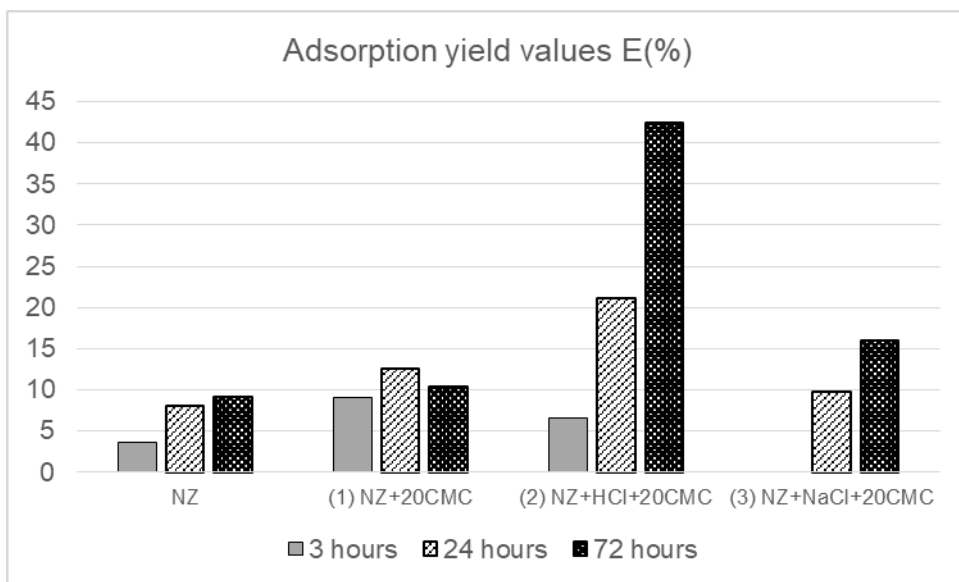
In order to have correct readings for the absorbance values, a time consuming procedure had to be followed for the separation of solid sorbent particles from the liquid phase. Solid sorbent particles of sizes within the 0.01 - 0.05  $\mu\text{m}$  fraction disperse in aqueous solution, cannot be filtered by usual means. Hence, because of the "cloudiness" of the solution, reproductibility of photometric measurements is affected.

Thus, simple filtration of permanganate solutions containing zeolite powder, in order to determine the residual anion concentration, is not a good option since: (1) permanganate is retained by the filter, hence altering experimental results, and (2) filters with very small pore sizes must be employed, unnecessarily prolonging the filtration time (allowing further contact between the liquid and the solid phase, thus continuous sorption during filtering, and hence producing altered results). Moreover, paper should not be used for filtration, since permanganate gets reduced to Mn(II), probably by oxidizing some of its organic constituents.

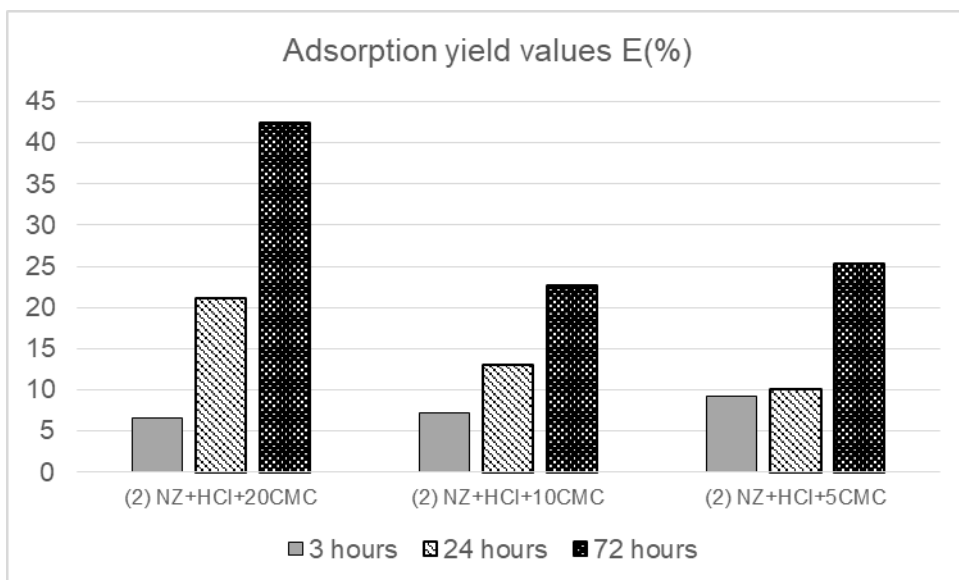
Therefore, separation of the liquid phase from the solid during sorption experiments was carried out by successive centrifugation. By using a simple water – NZ mixture, a number of at least 4 to 5 successive stages were necessary to reach the same photometric results (absorbance value at 525 nm) as those of demineralized water. Hence, we standardized the procedure of solid – liquid separation to 7 successive centrifugation steps (see also the Experimental section).

The sorption performance of different sorbents was assessed *via* a yield percentage **E** as defined by equation (2), where  $C_0 = 10 \text{ mg/L}$  stands for the initial permanganate concentration. Other performance indicators are also mentioned in the literature, for example the adsorption capacity, expressed as the adsorbed species / adsorbent mass ratio (usually in mg/g) [6]. However, all derive from the value of **C** in equation (1).

$$\mathbf{E} = 100 (C_0 - \mathbf{C})/C_0 \quad (2)$$



**Fig. 2.** Values of sorption yield E as a function of NZ modification type and total contact time between solid and liquid phases.



**Fig. 3.** Values of sorption yield E as a function of DDDBA concentration during chemical modification and total contact time between solid and liquid phases, for type (2) modified NZ.

Figures 2 and 3 present the values of sorption yields **E** for sorbents presented in Table 1, at three different total contact times between solid and liquid phases. Figure 2 compares performances of sorbents obtained by different treatment, whereas Figure 3 only the ones of type (2) having different specific surfaces and pore volumes.

At room temperature the process is quite slow and probably has not reached equilibrium even after 3 days (72 hours). A longer contact time generally brings about a higher yield, even in the case of unmodified NZ. The best adsorption capacity is seemingly proven by type (2) modified NZ, for long-term exposure. On the other hand, type (1) treatment proves to be more effective if a short-term process is targeted (see **E** values at 3 h in Figure 2). Type (3) surface modification is not recommended since it shows some sorption only after 24 or 72 hours, and even so the values of **E** are lower than in other cases. These findings are in agreement with the results in Table 1 (a higher specific surface and pore volume will favor adsorption).

Surprisingly, results in Figure 3 contradict expectations drawn from Table 1, namely that the highest specific surface obtained within the type (2) modified NZs ought to present the best yield. This might be due to the fact that results in Table 1 are based on nitrogen adsorption, a much smaller molecule than the permanganate ion, thus, even though there is a much larger surface available for adsorption processes, this is located mainly in the pores and therefore not accessible for large sized entities such as  $\text{MnO}_4^-$ .

Figure 3 further demonstrates that short-term performances (**E** values at 3 hours) are comparable, whereas the higher CMC concentration of the DDAB surfactant during preparation generates much better long-term yields (**E** values at 24 and 72 hours). Results at 5 and 10 CMC DDAB concentrations are comparable on the long-term, yet not as good as those for 20 CMC.

Results in Figures 2 and 3 are to be considered as preliminary findings. A more thorough study is necessary to draw pertinent conclusions of economic and technologic value. Experiments need repetition, control of temperature and study of its effect on the sorption performance. Modified NZ sorbents need exhaustive structural and surface characterization as well as the assessment of changes as a result of different preparation techniques. However, these results prove that the Kazakh originated natural zeolite may be developed into a performant pollutant adsorbent for wastewater. Moreover, a path to follow for the enhancement of sorption capacity by chemical modification has been identified.



## CONCLUSIONS

Natural zeolite (NZ) of clinoptilolite type originating from the Almaty region of the Republic of Kazakhstan, has been chemically modified. This was carried out by means of di-dodecyl-dimethyl-ammonium bromide (DDAB) surfactant treatment of NZ – type (1). Types (2) and (3) were treated, prior to DDAB, with acid (HCl) or salt (NaCl), respectively.

Both modified and unmodified NZ display a wide range of particle size distribution. Chemical modification enhances the specific surface as well as the pore volume of the sorbent, but does not influence in the same way the sorption yield. The process is slow, yet short- and long-term effectiveness are affected by preparation procedures. However, the most promising results in terms of adsorption capacity, are exhibited by an NZ subjected to a combined HCl - DDAB chemical treatment.

Even though presented results are preliminary, the investigated Kazakh natural zeolite exhibits potential to develop into a well performing sorbent. Moreover, at least one way for the desired enhancement of sorption yield has been described.

## EXPERIMENTAL SECTION

### Materials and chemicals

The natural zeolite (NZ) used in this work comes from the Shankanai deposit of Almaty region, Republic of Kazakhstan. The employed surfactant was the water-soluble di-dodecyl-dimethyl-ammonium bromide (DDAB). Other reactants were hydrochloric acid, sodium chloride and potassium permanganate. All reactants were of analytical grade and provided by Aldrich Chemistry, Germany. Experiments were carried out with demineralized water.

### Preparation of sorbents

Modified zeolite-based sorbents were prepared by different treatments applied to the natural form, as detailed below.

#### Type (1) sorbent, code: NZ + DDAB.

In this case, surface modification was achieved only by means of the surfactant. DDAB concentrations of 5, 10, and 20 CMC were used, where 1 CMC (critical micelle concentration) stands for 0.1 mM. In order to differentiate

among similar samples, the employed micellar concentration is indicated within the code.

A portion of 10 g of NZ was mixed at room temperature, in a glass conic flask, with 200 ml of DDAB aqueous solution, under continuous stirring at 500 rot/min (F20 Falc magnetic stirrer), for 24 hours. Then, the zeolite was separated by vacuum filtration, rinsed with 100 ml demineralized water, and dried at 60-70 °C in a SNOL 120-300LSN11 oven.

Type (2) sorbent, code: NZ + HCl + DDAB.

In this case, 20 g of NZ were mixed with 250 ml of 6 M HCl solution, for 2 hours and at 100 °C. Then, the solid zeolite was separated from the liquid phase by means of filtration and further rinsed with water until the pH of the rinsing water reached the value 7. The separated solid phase was dried at 70-80 °C for 4 hours. DDAB treatment was further applied as described for the type (1) sorbent.

Type (3) sorbent, code: NZ + NaCl + DDAB.

This sorbent was prepared according to the recipe described for type (2), but instead of hydrochloric acid, a 1 M NaCl solution was used, for 12 hours and at room temperature.

Both NZ and modified NZ were grained manually in a porcelain mortar. The obtained powder was further employed as such in sorption experiments.

## **Sorbent characterization**

The specific surface area and pore volume of sorbents were determined by nitrogen sorption up to its relative pressure of 0.2 atm, at -196 °C, on a Quantachrome NOVA 4200e device.

Particle size and distribution were assessed with the aid of a Shimadzu SALD-7101 powder analyzer.

## **Sorption experiments**

Sorption experiments were carried at approximately 20 °C room temperature, without any means of controlling it. Each experiment was started in the same way, by adding under continuous stirring a portion of 0.5 grams sorbent to a 500 ml potassium permanganate solution of 10 mg/L concentration. The entire volume (in a glass beaker) was continuously stirred at 500 rot/min by means of a F20 Falc magnetic stirrer.

After predetermined periods of time (3, 24 and 72 hours respectively), 10 ml aliquots were extracted from the bulk phase by using a pipette. In order to eliminate the fine dispersed solid particles from the solution with the aim of reproducible spectrophotometric measurements, the aliquots were centrifuged 7 times successively in glass tubes. Each centrifugation stage was carried out for 10 min at 3500 rot/min, by using a NAHITA 2610 centrifuge. After each such stage, the supernatant was collected and subjected to the next centrifugation step. The supernatant of the last stage was used to determine the unabsorbed permanganate concentration, at 525 nm, by means of double-beam 530 ABL&E-JASCO UV/VIS spectrophotometer. Quartz cuvettes of 1 cm optical path length were used. The reference cuvette contained demineralized water.

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