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Research Article

Adsorption of BTEX on Surfactant Modified Granulated Natural Zeolite Nanoparticles: Parameters Optimizing by Applying Taguchi Experimental Design Method

In this paper, a novel adsorbent developed by means of granulating of natural zeolite nanoparticles (*i.e.*, clinoptilolite) was evaluated for possible removal of the petroleum monoaromatics (*i.e.*, benzene, toluene, ethylbenzene, and xylene, BTEX). To do this, the natural zeolite was ground to produce nanosized particulate, then modified by two cationic surfactants and granulated. The effect of various parameters including temperature, initial pH of the solution, total dissolved solids (TDS), and concentration of a competitive substance (*i.e.*, methyl *tert*-butyl ether, MTBE) were studied and optimized using a Taguchi statistical approach. The results ascertained that initial pH of the solution was the most effective parameter. However, the low pH (acidic) was favorable for BTEX adsorption onto the developed adsorbents. In this study, the experimental parameters were optimized and the best adsorption condition by determination of effective factors was chosen. Based on the S/N ratio, the optimized conditions for BTEX removal were temperature of 40°C, initial pH of 3, TDS of 0 mg/L, and MTBE concentration of 100 μg/L. At the optimized conditions, the uptake of each BTEX compounds reached to more than 1.5 mg/g of adsorbents.

Keywords: Adsorption; BTEX; Granulated nanozeolite; Optimization; Surfactant-modified adsorbents; Taguchi method

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1 Introduction

Petroleum monoaromatics (benzene, toluene, ethylbenzene, and xylene isomers or briefly BTEX) are a group of hazardous environmental contaminants which originate from industrial sources such as refineries, gas, and oil extraction fields, petrochemicals and paint and glue industries. The BTEX polluted water resources especially groundwater resources represent a serious pollution problem because of high carcinogenetic effects [1, 2]. Hence, the presence of these compounds in water resources is undesirable and it is essential to remove them with feasible methods.

Amongst the most commonly used methods for the treatment of wastewaters, adsorption on activated carbon has gained prominence to remove a broad range of organic and inorganic pollutants. However, high costs of activated carbon and 10–15% loss during regeneration have limited vast use of activated carbon. This has led to a search for cheaper and more eco-friendly adsorbents. Zeolites and especially clinoptilolite family are among the alternatives that are available in plenty. Clinoptilolite is a family group of zeolites which due to its natural cation exchange capacities can be converted to anion exchanger and/or organic adsorbent, by cationic surfactants modification. The presences of huge resources of natural clinoptilolite zeolite in Iran make them easily accessible for the utilization in different application including wastewater treatment processes [3].

Possible application of natural clinoptilolite in wastewater treatment processes has been studied extensively for ammonia adsorption [4, 5], heavy metals uptake [6–8], and for removal of a broad range of volatile organic compounds (VOCs) including BTEX compounds [9, 10] in batch mode and fixed bed reactors.

This research group's previous study [11] showed that adsorbents based surfactant modified natural clinoptilolite can be considered as promising materials for removal of BTEX compounds. In addition by further grinding of natural clinoptilolite to finer nanosized particulates; its surface area will be increased remarkably. Furthermore, granulated natural zeolite nanoparticles exhibit a drastically increase in the adsorption capacity toward BTEX compounds [12, 13]. The pseudo-second-order kinetic represented the equilibrium data very well. An increase in temperature was found to induce a positive effect on the sorption process [11].

The effective diffusion coefficient of the BTEX onto the *n*-cetylpyridinium bromide (CPB)-modified granulated nanozeolite was in the order of 5.07E−12 m^2/s [12].

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Abbreviations: **ANOVA**, analysis of variance; **BTEX**, benzene, toluene, ethylbenzene, and xylene; **CPB**, *n*-cetylpyridinium bromide; **HDTMA-Cl**, hexadecyltrimethylammonium-chloride; **MTBE**, methyl *tert*-butyl ether; **TDS**, total dissolved solids

Recent studies on the thermodynamic of BTEX adsorption reaction revealed that Langmuir isotherm best represented the equilibrium adsorption of compounds onto surfactant modified nanozeolite. The results showed that the surfactant modified nanozeolite possessed heterogeneous surface with sorption sites having different activities.

Water resources generally experience thermal, physical, and chemical changes. On the other hand, there are other compounds in gasoline and petroleum solutions which can compete with BTEX compounds in adsorption process. Methyl *tert*-butyl ether (MTBE) is one these compounds, which is one of the hazardous pollutants [14].

Therefore, it is essential to study the simultaneous effects of different environmental conditions (temperature, pH, dissolved minerals, and MTBE presence). These parameters need to be optimized for attaining maximum sorptive removal of the adsorbate.

Taguchi is a simple and effective statistical method, which organizes a systematic experimentation to determine the near to optimum settings of design parameters for performance, quality, and cost. In this method, a large number of variables are studied with a small number of experiments using orthogonal arrays [15–20].

In the Taguchi approach, an orthogonal arrays and analysis of variance (ANOVA) are used for the analysis of experimentations. By using ANOVA, the effect of factors can be estimated and by orthogonal arrays the minimum number of experiments is needed. In this method variability of parameters is expressed by signal-to-noise (S/N) ratio, which represents the ratio of desirable results (signal) to undesirable results (noise). In this statistical method the S/N ratio is used to measure the quality characteristic derivation from the desired value. The maximum S/N ratio is considered as the optimal condition as the variability is inversely proportional to the S/N ratio [21].

Taguchi method has been used for devising a suitable strategy to perform experiments as well as for quality control purposes in optimized conditions. Optimizing of different adsorption process for environmental applications researches has been accomplished by applying this method [22–28]. Basically, the Taguchi experimental design is used to get information such as main effects of design parameters from minimum number of experiments.

The reduction of particle size of porous materials make larger external surface areas and shorter diffusion path lengths that reduce mass and heat transfer resistance in adsorption processes, decreasing of side reaction, increasing selectivity. Size reduction of porous zeolitic materials particularly to nanometer scales can drastically increase the adsorption capacity. However, direct use of nanozeolite powder in water treatment and other industrial processes is impossible due to the huge pressure drop associated with fine particles and the possibility of nanoparticles escaping into the environment. Consequently, the granulation approach has been chosen for application of nanozeolites in this study. The possibility of removal of BTEX compounds from contaminated synthetic water samples was investigated in a batch mode system by means of two adsorbents based on surfactant-modified granulated natural zeolitic nanoparticles. Uptake rate (*i.e.*, reaction kinetic) of BTEX adsorption is the key factor for evaluating the performance of the considered adsorbents. The Taguchi experimental design method was used to determine optimum removal conditions The effect of experimental parameters such as temperature, pH, total dissolved solids (TDS), and MTBE concentration were investigated using an L9 (34) orthogonal array. One of the main objectives of this research was to apply Taguchi statistical approach to optimize the reaction parameters toward higher adsorption rate. The adsorption efficiency of the prepared nanozeolitic adsorbents at optimized conditions was also investigated.

2 Experimental

2.1 Materials

All chemicals used in this research were purchased from Merck except sodium alginate powder which was obtained from Sigma–Aldrich Company and the natural zeolite was from a local mine. The entire chemicals were used as received without further pretreatments except the natural zeolite. The clinoptilolite-rich tuff employed in this study was a natural zeolite from the Miyaneh region (Azarbayjan province, North West of Iran). Detailed physico-chemical characterization of this mineral has already been presented in previous publications [29, 11]. Hexadecyltrimethylammonium-chloride (HDTMA-Cl; 50 wt% aqueous solution) and CPB; powder were used as cationic surfactants to modify the surface of the natural zeolite nanoparticles. Monoaromatic compounds (*i.e.*, BTEX) were chosen of GC grade chemicals. Dichloromethane was used for the cleansing of contact vials and other glassware.

The initial pH of the adsorbate solution was adjusted using 1 N (36.5 g/L) HCl or 1 N (40 g/L) NaOH aqueous solution without any further adjustment during the sorption process. The TDS concentration was adjusted by adding appropriate amounts of $CaCO_3$. The TDS of solutions was measured using a TDS meter (WTW, Cond 3301; Germany).

2.2 Preparation of adsorbents

In order to prepare zeolite nanoparticles from natural clinoptilolite, a ball mill (PM100, RETSCH GmbH) was used at two stages. In dry milling stage, 50 g of zeolite was milled with 10 balls for 10 min at 500 rpm and for wet milling, 50 g of zeolite was milled with 450 g of balls for 3 h at 450 rpm and 50 mL of water. The optimized milling approach suitable for the studied clinoptilolite and some of the results achieved are presented in one of our previous publications [30].

Preparing of granulated nanoparticles took place according to a protocol developed and reported before [31]. Zeolite nanoparticles were blended with clay and alginate gel (2% weight), this mixture was then dripped to 0.1 M barium chloride solution. Two hours later the granules were separated and washed with distilled water. To decompose and remove the alginate, the granules were calcined at 500°C for 5 h. To compare the results of natural particles and granulated nanoparticles, granules size between 590 and 840 μm (*i.e.*, in the same range of natural zeolite particulates) was then chosen for adsorption tests. Granulated nanoparticles were washed several times with tap water and then soaked in de-ionized water for 24 h to remove soluble salts and impurities prior to the BTEX adsorption tests. Samples were then dried over night and calcinated at 250°C for 24 h. In order to convert the natural zeolite sample (that was rich in calcium) to the sodium form, the adsorbent kept in contact with a 2 M solution of sodium chloride for 72 h and then completely rinsed with de-ionized water [32]. Argentometric tests were used to make sure there was no chloride in the modified samples [9]. The samples were then air dried for 48 h and stored in a sealed container over saturated sodium chloride solution in order to keep their water content fixed.

To modify the surface of the natural zeolite nanoparticles by the chosen cationic surfactants, in 125 mL polyethylene bottles, 3 g of the as-prepared sodium form nanozeolite granule was contacted with 100 mL of the surfactant solution with a concentration of 200 mmol/kg. The bottles were then agitated gently with a reciprocal shaker at 120 rpm for 48 h. Surface modified samples were then filtered and washed with excess de-ionized water. The prepared surface-modified adsorbents were air dried for 72 h and stored in gas tight polyethylene bottles in refrigerator (*i.e.*, 4°C). Table 1 presents the different types of adsorbents used in this study and their abbreviations.

2.3 BTEX adsorption tests

To prepare the BTEX stock solutions, 10 μL of each monoaromatic were added into a 100-mL volumetric flask using a precise 5-μL micropipette. As a result, concentration of monoaromatics in stock solution would be approximately 87 ppm (mg/L). The stock solution was mixed carefully by shaking the flask. The initial concentration of the stock solution was calculated from the density, purity, and volume of the monoaromatics used. The standard solution of BTEX was prepared by diluting of 10 mL of each stock solution in a 100-mL volumetric flask with de-ionized water achieving a solution containing 8.8, 8.7, 8.7, and 8.6 ppm of BTEXs, respectively. However, having the volatile nature of monoaromatic hydrocarbons and other losses and biases in the preparation process of solutions, the actual concentration of feed solution was measured by GC along with other solutions.

The adsorption experiments were performed according to the Taguchi statistical method applying the orthogonal array of an L9 type. The main operational parameters (factors) of the adsorption process were temperature, initial pH, TDS, and MTBE concentration. Details of the selected orthogonal are presented in Tab. 2.

In the Taguchi method, it is recommended to analyze the mean response for each run in the inner array and to analyze the variation using an appropriately chosen S/N ratio, which can be calculated by the following formula [33]:

$$\frac{\mathrm{S}}{\mathrm{N}} = -10\log\frac{\sum_i (1/Y_i^2)}{n} \tag{1}$$

where Y_i is the characteristic property and n is the replication number of the experiment. The S/N ratios are different according to the type of characteristics. In this research, the ''larger the better'' response is considered with the aim to maximize the BTEX removal [34].

The experimental data were processed with ''bigger-better'' quality characteristic (i) to determine the optimum conditions for the adsorption process, (ii) to identify significance of individual parameters for adsorption, and (iii) to estimate total monoaromatic uptake rate (q_e) at the optimum conditions. The details for analysis of experimental data are explained by many researchers [28, 35, 36].

An ANOVA was applied to the data in order to conduct an analysis of the relative importance of each factor more systematically. The used equations are the following:

$$S_T = \sum_{i=1}^{N} Y_i^2 - \frac{\tau^2}{N} \tag{2}$$

$$S_A = \left[\sum_{i=1}^{k_A}\left(\frac{A_i^2}{n_{A_i}}\right)\right] - \frac{\tau^2}{N} \tag{3}$$

$$v_T = N - 1 \tag{4}$$

$$v_A = k_A - 1 \tag{5}$$

$$V_A = \frac{S_A}{v_A} \tag{6}$$

where T is the sum of all observations, N is the total number of observations (in this case 9), A_i is the sum of observations under the A_i level, n_{A_i} is the number of observations under the A_i level, k_A is the number of levels of the factor A, S_T is the total sum of squares, S_A is the sum of squares for factor A (similar for the factors B, C, and D in this case), v_T is the total degrees of freedom, v_A is the factor A degrees of freedom, and finally V_A is the variance for the factor A [33, 37].

Calculations were performed with the Qualitek-4 (version 4.82.0, Nutek Inc) Software.

Table 1. The prepared surfactant modified adsorbent samples

Adsorbents	Surfactant used	Surfactant concentration (mmol/kg)	Abbreviation
Natural zeolite particles	HDTMA-Cl	200	SMZ#1
Natural zeolite particles	CPB	200	SMZ#2
Granulated zeolite nanoparticles	HDTMA-Cl	200	NSMZ#1
Granulated zeolite nanoparticles	CPB	200	NSMZ#2

Table 2. Process parameters for adsorption study of BTEX compounds using Taguchi method

	Parameters	Units	Levels		
			1	2	3
A	Temperature	°C	20	4	40
B	pH	–	7	3	11
C	TDS	mg/L	0	300	3000
D	MTBE	μg/L	0	100	1000

For each experimental run, a 10-mL aqueous solution, which was contained approximately 9 ppm of each BTEX compounds (*i.e.*, 8.8, 8.7, 8.7, and 8.6 for BTEXs, respectively) was added to 0.05 g of adsorbents (SMZ#1, SMZ#2, NSMZ#1, and NSMZ#2) in 20-mL amber glasses. These vessels were agitated at a constant shaking rate of 150 rpm in a incubator shaker (InnovaTM 4340, New Brunswick Scientific; China) maintained at 4, 20, or 40°C, as the case may be. The samples withdrawn after appropriate contact time with filtration and then the supernatant liquid was analyzed for the residual concentration of BTEX compounds.

The removal of monoaromatics from the solution and the equilibrium adsorption uptake in the solid phase, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{7}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of BTEX at initial and at equilibrium phase, respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

The concentration of BTEXs in the aqueous samples was determined by a gas chromatograph apparatus equipped with a flame ionization detector and a Combipal headspace auto sampler system (GC-FID; Model: CP-3800, Varian; Italy) from the difference between BTEX compounds concentration before and after the adsorption process. The detection limit of this system was 5 μg/L.

All the experiments took place in duplicate. The means standard deviation of the measured concentrations was ±0.002 ppm. A blank solution was used for eliminating the concentration losses due to vaporization of compounds, adsorbing to the wall of vessels, etc. The solution that resulted from the adsorption equilibrium after 48 h was separated from the saturated adsorbent by filtering and analyzed.

In order to verify the experimental results, certain confirmation experiments in duplicate were carried out at the optimum conditions.

3 Results and discussion

SEM micrographs of the micron sized parent natural clinoptilolite, the ground nanosized clinoptilolite produced by means of a developed planetary ball milling process, the macrosized granulated nanozeolite adsorbent, and the magnified surface image of granulated nanozeolite adsorbents showing nanoparticles of natural zeolite aggregated on the adsorbents granules) are illustrated in Fig. 1.

The surfactant modified adsorbents (SMZ#1, SMZ#2, NSMZ#1, and NSMZ#2) were selected for the experiments of the adsorption of petroleum monoaromatics (BTEX) from synthetic aqueous solutions. The column assignment and the results obtained from each set as the total amount of monoaromatics adsorbed onto adsorbents, q_e are presented in Tabs. 3 and 4.

Tables 5 and 6 show the raw data for the average value of q_e and S/N ratio for each parameter at the three levels, respectively, which were performed in duplicate. By comparing these results it can be concluded that the granulated nanosized adsorbents exhibit considerably better efficiency comparing to the natural parents. Furthermore, the CPB modified adsorbents show higher adsorption capacity in comparison to the HDTMA-Cl modified adsorbent which is in accordance with our previous studies [11–13]. The combination of factors in the experiments 8, 2, and 5, in which the q_e was the highest, showed the best adsorption results. It is found that the temperature and pH in the examined ranges showed remarkable affect on the q_e values. These data ascertained that the higher temperature of 40°C influenced the removal of BTEX more than the other studied factors. The pH also shows strong influence on

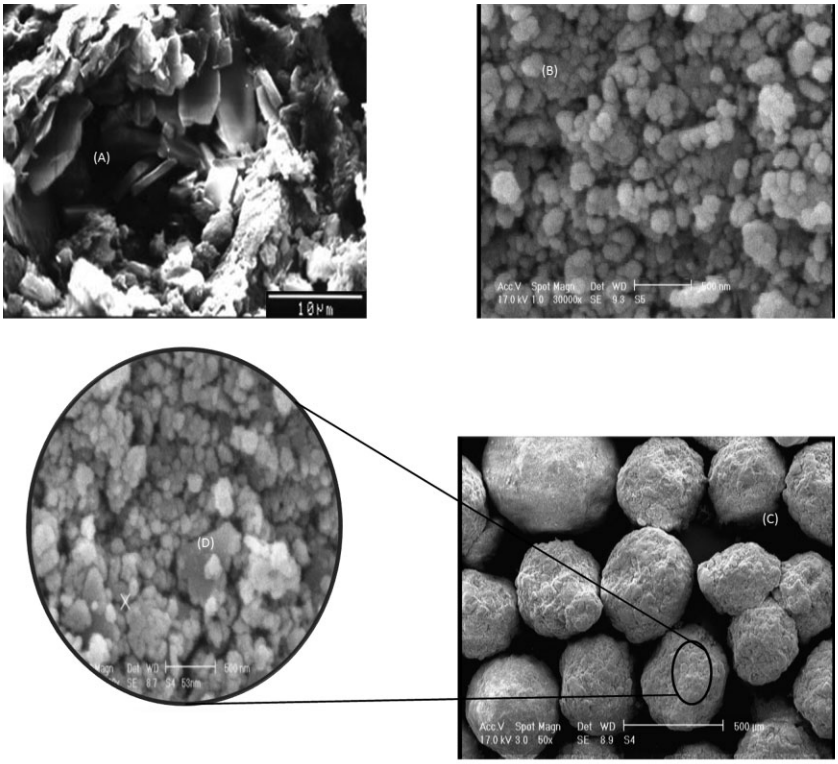

Figure 1. SEM micrographs of the micron sized parent clinoptilolite (A), ground nanosized clinoptilolite (B), the macrosized granulated nanozeolite adsorbent (C), and the nanoparticles of the zeolite aggregated on the adsorbents granules (D).

Table 3. Column assignment for the various factors in the Taguchi's L9(3^4) orthogonal array and experimental q_e values for multi-component BTEX adsorption onto different adsorbents

Exp. No.	Temperature (°C)	pH	TDS (mg/L)	MTBE (μg/L)	SMZ#1				SMZ#2				NSMZ#1				NSMZ#2			
					q_e (mg/L)(average)				q_e (mg/L)(average)				q_e (mg/L)(average)				q_e (mg/L)(average)			
					B	T	E	X	B	T	E	X	B	T	E	X	B	T	E	X
1	20	7	0	0	0.256	0.226	0.184	0.17	0.357	0.332	0.286	0.272	1.116	0.854	0.692	0.626	1.176	0.904	0.732	0.670
2	20	3	300	100	0.776	0.608	0.452	0.418	0.794	0.74	0.674	0.522	1.338	1.218	0.964	1.096	1.450	1.104	1.032	1.192
3	20	11	3000	1000	0.072	0.088	0.052	0.060	0.166	0.116	0.072	0.146	0.810	0.522	0.394	0.374	0.952	0.660	0.434	0.326
4	4	7	300	1000	0.186	0.122	0.178	0.124	0.344	0.304	0.266	0.208	0.990	0.776	0.628	0.592	1.158	0.808	0.578	0.654
5	4	3	3000	0	0.664	0.424	0.372	0.340	0.69	0.61	0.61	0.486	1.316	1.048	0.812	0.914	1.412	1.068	0.952	1.066
6	4	11	0	100	0.042	0.024	0.046	0.052	0.034	0.032	0.056	0.044	0.728	0.506	0.326	0.208	0.808	0.640	0.414	0.322
7	40	7	3000	100	0.424	0.328	0.306	0.328	0.452	0.506	0.488	0.466	1.290	0.972	0.718	0.762	1.182	0.948	0.850	0.848
8	40	3	0	1000	0.940	0.856	0.622	0.514	0.902	0.84	0.842	0.85	1.538	1.360	1.062	1.250	1.518	1.13	1.228	1.388
9	40	11	300	0	0.134	0.104	0.116	0.106	0.33	0.13	0.10	0.15	0.942	0.686	0.430	0.504	1.046	0.772	0.480	0.460

Table 4. Column assignment for the various factors and S/N ratio for BTEX adsorption onto different adsorbents

Exp. No.	Temperature (°C)	pH	TDS (mg/L)	MTBE (μg/L)	SMZ#1				SMZ#2				NSMZ#1				NSMZ#2			
					S/N ratio				S/N ratio				S/N ratio				S/N ratio			
					B	T	E	X	B	T	E	X	B	T	E	X	B	T	E	X
1	20	7	0	0	−11.839	−12.944	−14.729	−15.42	−8.947	−9.578	−10.874	−11.32	0.953	−1.371	−3.198	−4.069	1.408	−0.877	−2.711	−3.48
2	20	3	300	100	−2.205	−4.323	−6.898	−5.578	−2.006	−2.616	−3.428	−5.65	2.528	1.712	−0.323	0.796	3.224	0.859	0.272	1.525
3	20	11	3000	1000	−22.854	−21.111	−25.758	−24.495	−15.6	−18.746	−22.854	−16.716	−1.831	−5.647	−8.092	−8.546	−0.428	−3.61	−7.251	−9.738
4	4	7	300	1000	−14.612	−18.277	−14.992	−18.132	−9.271	−10.345	−11.506	−13.65	−0.088	−2.204	−4.042	−4.555	1.274	−1.854	−4.763	−3.689
5	4	3	3000	0	−3.558	−7.454	−8.591	−9.373	−3.226	−4.294	−4.296	−6.269	2.385	0.406	−1.809	−0.782	2.996	0.57	−0.428	0.553
6	4	11	0	100	−27.565	−33.22	−26.745	−25.854	−29.371	−30.721	−25.053	27.565	−2.758	−5.918	−9.736	−13.64	−1.854	−3.879	−7.66	−9.848
7	40	7	3000	100	−7.458	−9.691	−10.291	−9.7	−6.898	−5.921	−6.232	−6.634	2.211	−0.247	−2.878	−2.363	1.451	−0.465	−1.412	−1.435
8	40	3	0	1000	−0.538	−1.351	−4.125	−5.786	−0.897	−1.517	−1.494	−1.412	3.739	2.67	0.522	1.938	3.625	1.061	1.783	2.847
9	40	11	300	0	−17.47	−19.665	−18.808	−15.095	−9.595	−17.725	−20.355	−16.5	−0.52	−3.277	−7.334	−5.953	0.389	−2.248	−6.384	−6.746

the q_e comparing to the other parameters. With an increase in the pH from 3 to 11 the values of q_e decrease sharply.

The response curves for the individual effects of various parameters on q_e are given in Fig. 2 (only NSMZ#2). An increase in the levels of temperature from 1 to 2 and from 2 to 3 resulting an increase in the q_e values, however it is reverse in the case of pH factor. This is in accordance to our previous study [11].

Influence of temperature on q_e can be due to mobility increase of adsorbate in the adsorbent matrix which enhances the adsorption uptake rate [38]. On the other hand, an increase in the adsorption

Table 5. Average and main effect values of q_e for different adsorbents

Adsorbent	Factor	Benzene			Toluene			Ethylbenzene			Xylenes		
		Raw data (average)			Raw data (average)			Raw data (average)			Raw data (average)		
		L1	L2	L3	L1	L2	L3	L1	L2	L3	L1	L2	L3
SMZ#1	*T*	0.368	0.297	0.499	0.307	0.189	0.429	0.229	0.198	0.347	0.216	0.171	0.316
	pH	0.288	0.793	0.082	0.225	0.629	0.072	0.222	0.481	0.071	0.207	0.424	0.072
	TDS	0.412	0.365	0.386	0.368	0.277	0.28	0.284	0.248	0.243	0.245	0.216	0.242
	MTBE	0.351	0.414	0.399	0.251	0.319	0.355	0.223	0.268	0.284	0.205	0.266	0.232
SMZ#2	*T*	0.439	0.356	0.561	0.395	0.315	0.491	0.344	0.31	0.476	0.313	0.246	0.488
	pH	0.384	0.795	0.176	0.38	0.73	0.092	0.346	0.708	0.075	0.315	0.619	0.113
	TDS	0.43	0.489	0.435	0.401	0.391	0.41	0.394	0.346	0.39	0.388	0.293	0.365
	MTBE	0.458	0.426	0.47	0.357	0.425	0.419	0.332	0.406	0.393	0.302	0.343	0.401
NSMZ#1	*T*	1.087	1.011	1.256	0.864	0.776	1.007	0.683	0.588	0.736	0.698	0.571	0.837
	pH	1.131	1.397	0.825	0.867	1.208	0.572	0.679	0.946	0.383	0.66	1.086	0.36
	TDS	1.127	1.089	1.138	0.906	0.894	0.847	0.693	0.674	0.641	0.694	0.729	0.683
	MTBE	1.124	1.118	1.112	0.864	0.898	0.885	0.644	0.669	0.694	0.68	0.688	0.738
NSMZ#2	*T*	1.192	1.126	1.25	0.889	0.838	0.946	0.732	0.648	0.852	0.729	0.68	0.898
	pH	1.172	1.46	0.936	0.886	1.1	0.689	0.719	1.07	0.442	0.723	1.215	0.369
	TDS	1.167	1.219	1.182	0.891	0.893	0.891	0.791	0.696	0.745	0.793	0.768	0.746
	MTBE	1.212	1.146	1.209	0.913	0.897	0.865	0.721	0.765	0.746	0.732	0.787	0.789

Table 6. S/N data of BTEX adsorption onto different adsorbents

Adsorbent	Factor	Benzene S/N data			Toluene S/N data			Ethylbenzene S/N data			Xylenes S/N data		
		L1	L2	L3	L1	L2	L3	L1	L2	L3	L1	L2	L3
SMZ#1	*T*	−12.299	−15.245	−8.489	−12.792	−19.65	−10.236	−15.795	−16.776	−11.075	−15.831	−17.786	−11.667
	pH	−11.303	−2.1	−22.63	−13.637	−4.376	−24.665	−13.337	−6.538	−23.77	−14.418	−7.579	−23.288
	TDS	−13.314	−11.429	−11.29	−15.838	−14.088	−12.752	−15.2	−13.566	−14.88	−15.687	−15.074	−14.523
	MTBE	−10.956	−12.409	−12.668	−13.354	−15.744	−13.58	−14.043	−14.645	−14.958	−14.769	−14.378	−16.138
SMZ#2	*T*	−8.851	−13.956	−5.797	−10.313	−15.12	−8.387	−12.385	−13.618	−9.361	−11.229	−15.828	−8.182
	pH	−8.372	−2.043	−18.189	−8.615	−2.809	−22.397	−9.537	−3.073	−22.754	−10.535	−4.444	−20.26
	TDS	−13.072	−6.957	−8.575	−13.939	−10.229	−9.654	−12.474	−11.763	−11.127	−13.432	−11.933	−9.873
	MTBE	−7.256	−12.758	−8.589	−10.532	−13.086	−10.203	−11.482	−11.571	−11.951	−11.363	−13.283	−10.593
NSMZ#1	*T*	0.55	−1.54	1.81	−1.769	−2.572	−0.285	−3.871	−5.196	−3.23	−3.94	−6.326	−2.126
	pH	1.025	2.884	−1.703	−1.274	−1.596	−4.947	−3.373	−0.537	−8.387	−3.662	0.651	−9.38
	TDS	0.644	0.64	0.921	−1.54	−1.256	−1.829	−4.138	−3.899	−4.26	−5.257	−3.237	−3.897
	MTBE	0.939	0.661	0.607	−1.414	−1.484	−1.727	−4.114	−4.312	−3.871	−3.601	−5.069	−3.721
NSMZ#2	*T*	1.401	0.805	1.822	−1.209	−1.721	−0.551	−3.23	−4.284	−2.004	−3.898	−4.328	−1.778
	pH	1.377	3.282	−0.631	−1.066	0.83	−3.246	−2.962	0.542	−7.098	−2.868	1.642	−8.777
	TDS	1.059	1.629	1.34	−1.232	−1.081	−1.168	−2.863	−3.625	−3.03	−3.494	−2.97	−3.54
	MTBE	1.598	0.94	1.49	−0.852	−1.162	−1.468	−3.174	−2.933	−3.41	−3.224	−3.253	−3.527

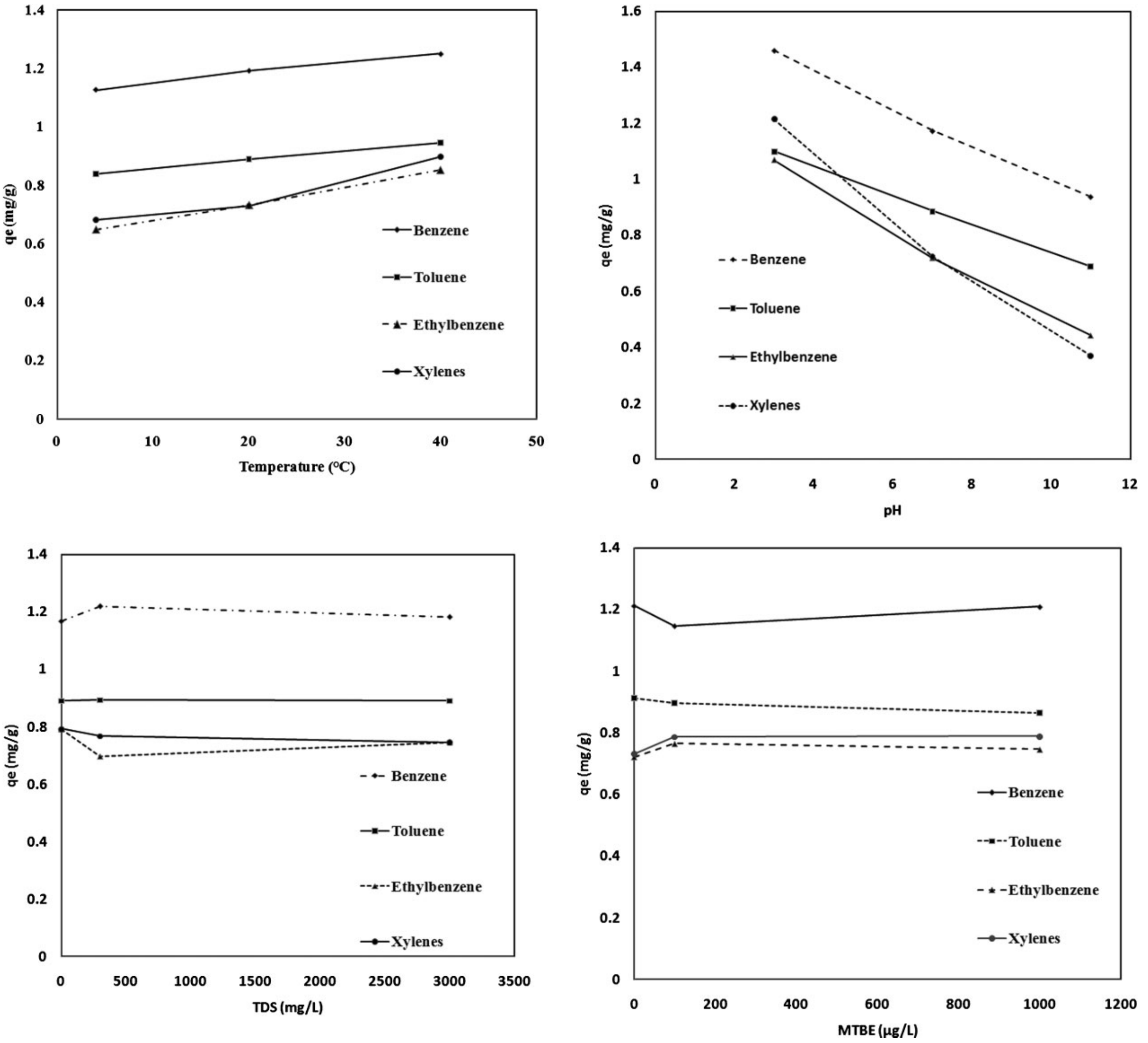

Figure 2. Effect of different process parameters on q_e for multi-component adsorption of BTEX on NSMZ#2 sample.

Table 7. Analyze of ANOVA for BTEX adsorption onto adsorbents in this study (un-pooled) (S/N ratio)

Adsorbent	Factor	DOF (*f*)	Benzene			Toluene			Ethylbenzene			Xylenes		
			SS	V	P (%)	SS	V	P (%)	SS	V	P (%)	SS	V	P (%)
SMZ#1	*T*	2	68.843	34.421	9.613	142.208	71.104	18.091	55.748	27.874	10.854	58.62	29.31	13.384
	pH	2	634.451	317.225	88.6	619.034	309.517	78.75	452.036	226.018	88.016	372.199	186.099	84.98
	TDS	2	7.67	3.835	1.071	14.375	7.187	1.828	4.496	2.248	0.875	2.034	1.017	0.464
	MTBE	2	5.112	2.556	0.713	10.45	5.225	1.329	1.298	0.649	0.252	5.126	2.563	1.17
	Error	0												
	Total	8	716.077		100.00	786.069		100.00	513.581		100.00	437.98		100.00
SMZ#2	*T*	2	101.968	50.984	16.751	72.149	36.074	9.925	28.798	14.399	4.531	88.895	44.447	17.728
	pH	2	397.098	198.549	65.234	607.374	303.687	83.554	603.829	301.914	95.004	381.839	190.919	76.152
	TDS	2	60.223	30.111	9.893	32.456	16.228	4.464	2.721	1.36	0.428	19.164	9.582	3.822
	MTBE	2	49.432	24.716	8.12	14.942	7.471	2.055	0.229	0.114	0.036	11.516	5.758	2.296
	Error	0												
	Total	8	608.723		100.00	726.922		100.00	635.579		100.00	501.416		100.00
NSMZ#1	*T*	2	5.937	2.968	15.535	8.08	4.04	11.026	6.029	3.014	5.949	26.622	13.311	14.095
	pH	2	31.936	15.968	83.556	64.548	32.274	88.08	94.816	47.408	93.561	151.899	75.949	80.423
	TDS	2	0.155	0.077	0.407	0.493	0.246	0.627	0.201	0.1	0.199	6.365	3.182	3.37
	MTBE	2	0.191	0.095	0.5	0.161	0.08	0.220	0.293	0.146	0.289	3.985	1.992	2.11
	Error	0												
	Total	8	38.221		100.00	73.283		100.00	101.341		100.00	188.872		100.00
NSMZ#2	*T*	2	1.566	0.783	6.077	2.064	1.032	7.474	7.806	3.903	8.057	11.181	5.59	6.361
	pH	2	22.969	11.484	89.138	24.956	12.478	90.34	87.772	43.886	90.597	163.815	81.907	93.201
	TDS	2	0.486	0.243	1.889	0.034	0.017	0.124	0.961	0.48	0.992	0.601	0.3	0.342
	MTBE	2	0.745	0.372	2.894	0.569	0.284	2.06	0.341	0.17	0.352	0.167	0.083	0.095
	Error	0												
	Total	8	25.768		100.00	27.625		100.00	96.882		100.00	175.765		100.00

capacity of BTEX compounds with an increase in temperature confirms dominative chemisorptions mechanism on BTEX adsorption by surfactant modified zeolites [12].

Figure 2 shows a decrease in q_e with an increase in the level of pH from 3 to 11. This could be due to the fact that the weak charge of monoaromatic compounds is maximum at low pH and there is a reduction of charge with increase of pH, which affects the uptake rate adversely [11, 39, 40]. In addition, the increase in concentrations of TDS and MTBE has minor effect on BTEX uptake rate, which indicates that the surfactant-modified adsorbents used in this study can be used effectively for BTEX adsorption process at various operational conditions.

The results reveal that the optimal conditions for the removal of BTEX are temperature at level 3 (*i.e.*, 40°C), pH at level 2 (*i.e.*, pH 3), TDS at level 1 (*i.e.*, 0 mg/L), and MTBE concentration at level 3 (*i.e.*, 1000 μg/L). As it is shown in Tab. 6, these conditions exhibit the highest S/N values for each factor. The results of the ANOVA are shown in Tab. 7.

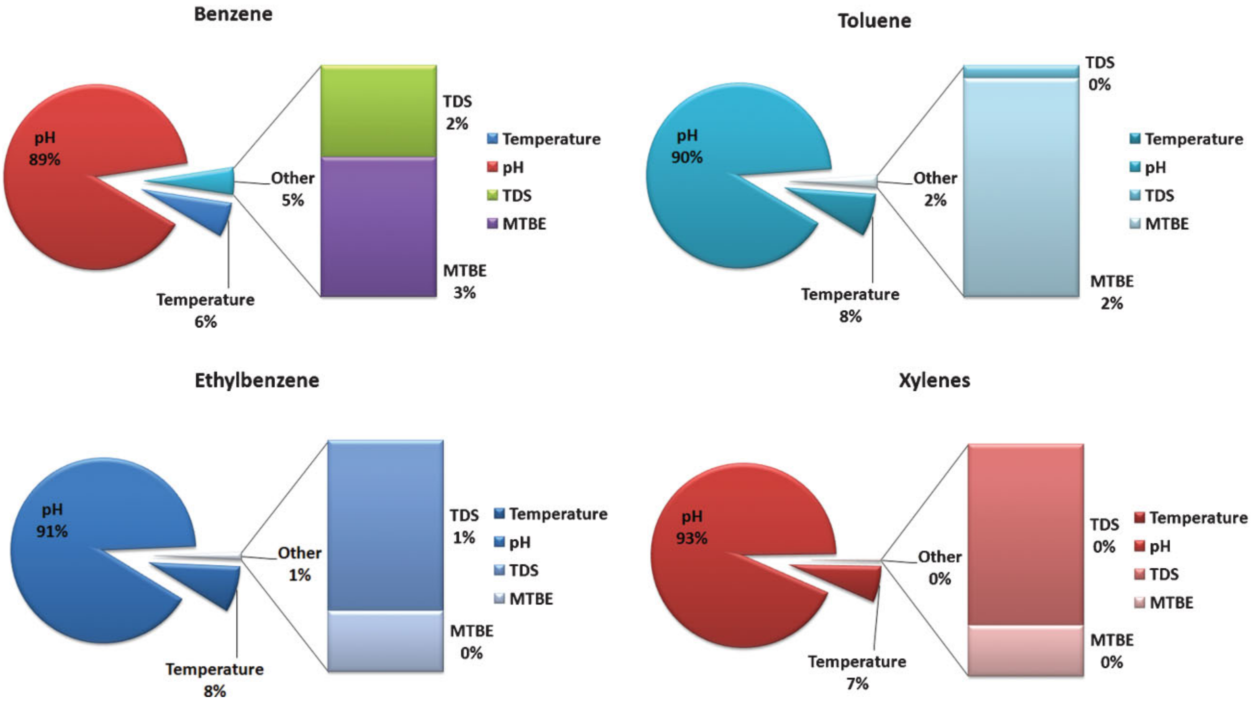

Figure 3. Contribution of parameters in adsorption of BTEX on NSMZ#2 sample.

Table 8. Optimum conditions if BTEX adsorption onto adsorbents in this study (S/N ratio-unpooled)

Adsorbent	Factor	Benzene			Toluene			Ethylbenzene			Xylenes		
		Level description	Level	Contribution	Level description	Level	Contribution	Level description	Level	Contribution	Level description	Level	Contribution
SMZ#1	*T*	40	3	3.522	40	3	3.99	40	3	3.473	40	3	3.428
	pH	3	2	9.91	3	2	9.85	3	2	8.01	3	2	7.515
	TDS	3000	3	0.721	3000	3	1.474	300	2	0.982	3000	3	0.571
	MTBE	0	1	1.055	0	1	0.871	0	1	0.505	100	2	0.717
	Expected result at optimum condition (q_e)		1.445			1.253			0.834			0.719	
SMZ#2	*T*	40	3	3.738	40	3	2.886	40	3	2.427	40	3	3.564
	pH	3	2	7.491	3	2	8.464	3	2	8.715	3	2	7.302
	TDS	300	2	2.577	3000	3	1.619	3000	3	0.66	3000	3	1.873
	MTBE	0	1	2.278	1000	3	1.070	100	2	0.216	1000	3	1.153
	Expected result at optimum condition (q_e)		2.125			1.375			1.027			1.28	
NSMZ#1	*T*	40	3	1.074	40	3	1.257	40	3	0.868	40	3	2.004
	pH	3	2	2.148	3	2	3.137	3	2	3.562	3	2	4.781
	TDS	3000	3	0.186	300	2	0.285	300	2	0.199	300	2	0.893
	MTBE	0	1	0.203	0	1	0.127	1000	3	0.228	0	1	0.529
	Expected result at optimum condition (q_e)		1.649			1.456			1.091			1.599	
NSMZ#2	*T*	40	3	0.479	40	3	0.609	40	3	1.168	40	3	1.556
	pH	3	2	1.939	3	2	1.99	3	2	3.714	3	2	4.976
	TDS	300	2	0.286	300	2	0.079	0	1	0.309	300	2	0.364
	MTBE	0	1	0.254	0	1	0.308	100	2	0.239	0	1	0.11
	Expected result at optimum condition (q_e)		1.641			1.234			1.297			1.526	

The most influential factor was the pH because the variance (*V*) was higher in comparison with the other factors. The temperature of the solution was the second factor and finally the TDS and MTBE concentrations. Considering the degree of freedom for the error (ve) term as 0 (calculated as the difference between the total degree of freedom and the accumulative degree of freedom of all factors), the variance of the error and consequently the *F*-ratio could not be calculated.

The contribution of individual factors is the key for the control to be enforced on the adsorption of BTEX. It can be observed from Tab. 7 that the pH is the most significant factor with approximately contribute up to 80% on the raw data for the BTEX adsorption.

The contribution of each parameter for q_e for NSMZ#2 is shown in Fig. 3. Since q_e is ''bigger-better'' type quality characteristic, greatest value of q_e is considered to be the optimal. The optimal level of various parameters obtained after examining the response curves (Fig. 2) of the average value of q_e, are summarized in Tab. 8. The predicted optimum value of q_e for adsorbents in this study as calculated from Eq. (2) is found to be approximately 1.5 mg/g for each compound.

The confirmation experiments were conducted for simultaneous adsorption of BTEX compounds onto surfactant modified adsorbents at selected optimal levels of the process parameters in duplicate. The results are given in Tab. 9. It shows that the results are higher than the results obtained during the initial experiments; however, all of them are lower than the predicted optimum results. Having the fact that the *F*-ratio cannot be calculated, the range of optimum results is not available.

4 Conclusions

In this research, natural zeolite nanoparticles were produced mechanically, formed as granule, and finally modified by cationic surfactant to develop new sorbents for BTEX uptake. A Taguchi L9

Table 9. Results of adsorption of BTEX onto adsorbents at the optimum conditions

Adsorbents	Factors' level				q_e (average value)			
	Temperature	pH	TDS	MTBE	Benzene	Toluene	Ethylbenzene	Xylenes
SMZ#1	40	3	3000	0	1.150	1.022	0.808	0.696
SMZ#2	40	3	3000	1000	1.426	1.162	0.988	0.974
NSMZ#1	40	3	300	0	1.518	1.298	1.006	1.190
NSMZ#2	40	3	300	0	1.586	1.244	1.160	1.188

design was used as a statistical tool in order to study the effects of different factors including temperature, pH, TDS, and MTBE concentrations on the adsorption of petroleum monoaromatics onto two granulated nanosized natural zeolite and their micron sized natural clinoptilolite adsorbents modified by two different cationic surfactants (*i.e.*, HDTMA-Cl and *n*-CPB).

The results obtained revealed that the produced nanosized clinoptilolite even after shaping in a granular form, exhibit drastically increased adsorption capacity (approximately 60% higher than the parent micron sized zeolite). In addition, the type of surfactant used for surface modification also has a significant effect on the BTEX adsorption process, where the CPB modified adsorbents showed more than 25% higher adsorption capacity comparing to the HDTMA modified samples. Having the experimental data obtained by mean of applying the Taguchi statistical approach, at the optimum conditions, the adsorption capacity of the modified granulated zeolitic nanoparticles can reach up to 1.6, 1.2, 1.16, and 1.2 mg/g of adsorbent for BTEXs, respectively. Removal of BTEX compounds by surfactant modified adsorbents was influenced by the different studied factors in the order: pH > temperature > TDS > MTBE for HDTMA-modified adsorbents; and pH > temperature > MTBE > TDS for CPB-modified adsorbents, which could be due to higher adsorption affinity of MTBE molecule towards CPB, compared to the BTEX molecules. The experimental results revealed that the developed granulated surfactant-modified nanozeolites are capable to adsorb BTEX molecules regardless of the presence of interfering compounds such as TDS and MTBE. It can be concluded that the developed adsorbents based on zeolitic nanoparticles can be considered as promising adsorbents for removal of the BTEX compounds from natural water resources, however, the removal process should be optimized by adjusting the pH and temperature of contaminated water streams. In addition to the effects of temperature and pH, which influencing the electrostatic interactions, having the fact of hydrophobic nature of BTEX organic molecules and surface of the developed surfactant modified zeolite as the adsorbent, the possibility of an entropy-driven process in the adsorption should be taken into consideration.

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