



## Research Article

# Immobilization of modified zeolite on polyethylene surface: characterization and its application toward phosphate removal and microalgae growth

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## Abstract

Herein, firstly zeolite was modified with Na<sup>+</sup> and Fe<sup>3+</sup> ions and then immobilized on polyethylene surface to construction of modified zeolite coated surface (MZCS). The prepared MZCS was characterized by using XRD, ATR-FTIR, SEM and EDXA techniques and its ability toward phosphate removal was examined and compared with unmodified zeolite coated surface (ZCS). Affecting parameters on phosphate removal were investigated and our results showed the ZCS and MZCS achieved to 32.4% and 70.6% phosphate removal ability after 2 h, for 25.0 ppm phosphate at pH 7.0, respectively. The phosphate adsorption results very well fitted in the Langmuir isotherm model for both the ZCS and MZCS. The maximum adsorption capacity as 6.317 and 7.097 mg/g was observed for the ZCS and MZCS, respectively. Finally, the application of the ZCS and the MZCS for phosphate removal from wastewater and its effect on microalgae growth was tested in two media with three replications. Observed results were presented and discussed here.

**Keywords** Modified surface · Phosphate adsorption · Wastewater · Coated surface

## 1 Introduction

Zeolite, boiling stone [1], is crystalline aluminosilicate with a tetrahedral framework. The structural composition of zeolite results micro-pores and cavities dimensions ranging from 0.3 to 2.0 nm [2, 3]. The molecular sieve, resulting from the high void volumes of zeolite, only allows molecules of a certain size (equal to, or less than the pore size) to pass through entry channels, whereas molecules larger than the pore size are excluded [4]. It provides the possibility of using zeolite in collecting and determining different species [5]. Replacing silicons by aluminum in a tectosilicate framework of zeolite, resulting a negative charge in the zeolite framework and consequently lead to bond alkaline or alkaline earth metals to its external surface of zeolite, electrostatically [6–8]. For example, adsorption of

cations like Cu<sup>2+</sup> [9], Fe<sup>3+</sup> [10], Co<sup>2+</sup> [11], and As<sup>3+</sup> [12], are reported in recent years.

Unlike the adsorption of cations, due to the exciting negative charge on the aluminosilicate framework of zeolite, the efficiency of anions adsorption is low. Therefore, in order to adsorb them, the zeolite surface must be modified by appropriate modifiers. Many investigations have been conducted on improve efficiency of separation and adsorption of anions by using different modifiers. This efforts can be divided to three groups: (1) treatment by acids or bases [13–16], (2) modification by surfactants such as; tetramethylammonium [17, 18], cetyltrimethylammonium [19, 20], hexadecyltrimethylammonium [21–25], octadecyldimethylbenzyl ammonium [19, 26, 27], n-cetylpyridinium [28] and polyhexamethyleneguanidine [29], and (3) modification by metal ions such as

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Fe<sup>3+</sup> [30]. For example, Hebuda-Stanic et al. [31] modified zeolite with Fe<sup>3+</sup> ions and investigated its ability in arsenic.

However, due to easy modification, ion exchange ability, molecular sieve property, low cost, and high purity of zeolite its applications in catalysis [10], medicinal [32], industrial [33], chemical sensing [9, 34], air separation [35], and removal of heavy metals [36] are more increased. One of the most important applications of zeolites is removal of pollutants from the water and wastewater [37]. The presence of different contaminants such as heavy metal ions [38], organic compounds [39, 40] and inorganic anions [41] in wastewater led to several types of health problems for the aquatic ecosystem. Inorganic anions contain several metalloids [24, 42], metal anions [43, 44] and several acid ions such as phosphate [45, 46] are present in large volume in the wastewaters.

In this study, the natural zeolite as a low-cost adsorbent was modified and coated to the polyethylene surface. Ability of the modified polyethylene, in phosphate removal from aqueous solution was studied and several techniques are used to trace the events occurred at the surface. The equilibrium studies were carried out and finally applicability of the surface was tested in reducing the algae growth rate in wastewater. Observed results analyzed and discussed here.

## 2 Experimental section

### 2.1 Reagents

Natural Clinoptilolite zeolite was obtained from a mine Semnan Province I.R. Iran. All chemicals were of analytical grade, obtained from Merck® company from Germany and used as supplied without further purification. A stock solution of phosphate (100.0 ppm) was made by the dissolution of 0.0358 g KH<sub>2</sub>PO<sub>4</sub> in 250 mL of double-distilled water. Dilute solutions of phosphate (25.0, 50.0 and 75.0 ppm) were prepared just before use from a stock solution. All glassware was cleaned with dilute nitric acid (10%) and rinsed several times with milli-Q ultrapure water before experiments.

### 2.2 Apparatus

The concentration of phosphate in the solution was determined spectrophotometrically at 400 nm by 2550 spectrophotometer, Shimadzu after an equilibrium time. A PerkinElmer 65 spectrometer was used for attenuated total reflectance Fourier transform infrared (ATR-FTIR) investigations and the spectra were obtained in the wave-number range of 400–4000 cm<sup>-1</sup>. A Philips pw 1800 instrument was used for X-ray diffraction (XRD) measurements and

the spectra were performed at a voltage of 60 kV and a current of 400 mA. Scanning electron microscopy (SEM) images and energy dispersive X-ray diffraction (EDX) were taken by XL30 Philips the Netherlands. An inverted microscope (Carl Zeiss Microscopy GmbH, Germany) coupled a digital camera was used to take images of cultured cells and the number of algae in images was counted by Neubauer chamber (0.0025 mm<sup>2</sup>, 0.100 mm Tiefe depth).

### 2.3 Modification of polyethylene surface by zeolites

Firstly, 1 g of natural zeolite was lightly ground and washed with deionized water and dried in the oven at 250 °C for 6 h. To prepare modified zeolite, it was pretreatment with 1.0 M NaCl to obtain Na-form zeolite for 24 h at room temperature followed by washing with deionized water until neutral pH and drying at 200 ± 2 °C. Na-form zeolite was placed in 100 mL 0.01 M FeCl<sub>3</sub> solution for 3 days at room temperature. Modified zeolite was separated by filtration, washed with deionized water and dried at room temperature. Then, the modified zeolite was dispersed in 2.5 mL tetrahydrofuran and 2.5 mL of styrene and a thin layer of this suspension was coated on polyethylene cube (1 × 1 × 5 cm) surface allowed to dry in the air for about 30 min to prepare MZCS. In the preparation of the ZCS, zeolite was used instead of modified zeolite. The schematic of the surface is represented in Scheme 1.

### 2.4 Phosphate adsorption on the surface

Accumulation of phosphate was performed by immersion of the MZCS in 50 mL 25.0 ppm phosphate solution, pH 7.0 using the bath equilibration technique for 2 h at 500 rpm and 25 ± 1 °C. After accumulation, the MZCS was removed, the phosphate concentration in solution was analyzed with the vanadomolybdo phosphoric acid colorimetric method [47, 48]. For comparison, all experiments were performed by the ZCS. Phosphate adsorption efficiency from solution on the ZCS and the MZCS was calculated according to Eq. 1:

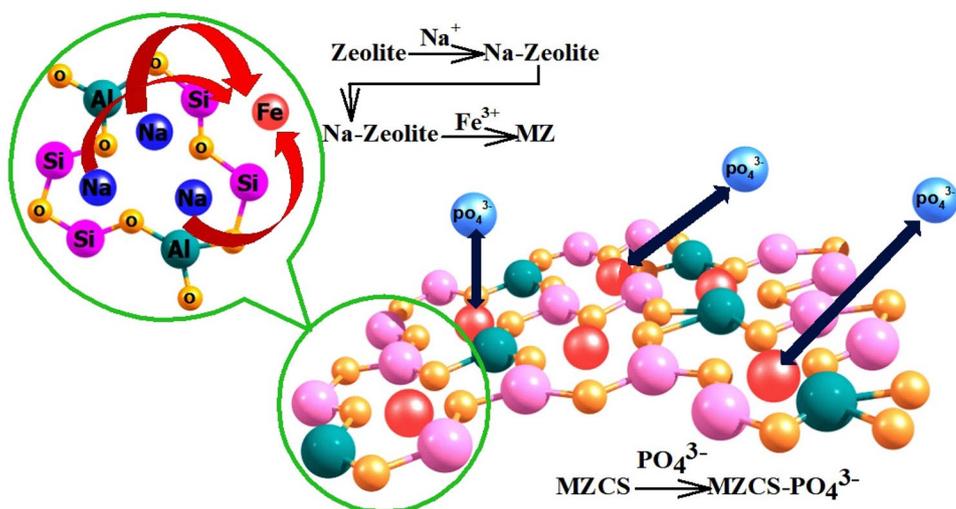
$$\text{Phosphate adsorption \%} = (C_i - C_f) \times 100 / C_i \quad (1)$$

where C<sub>i</sub> and C<sub>f</sub> are the blank and final concentration of phosphate in the solution (mg/g) after adsorption, respectively.

### 2.5 Wastewater algae growth experiments

The wastewater samples obtained from Isfahan Shahin-Shahr treatment plant and were selected as a culture medium. Three culture mediums were maintained under the same physiological conditions (temperature: 25 ± 1 °C, photoperiod: 16:8 and lightly intensity: 2500 ft-c). After

**Scheme 1** Schematic of the ZMCS and its application in phosphate adsorption



30 days, the number of algae cells per mL of wastewater was counted using a microscope and Neubauer chamber [49].

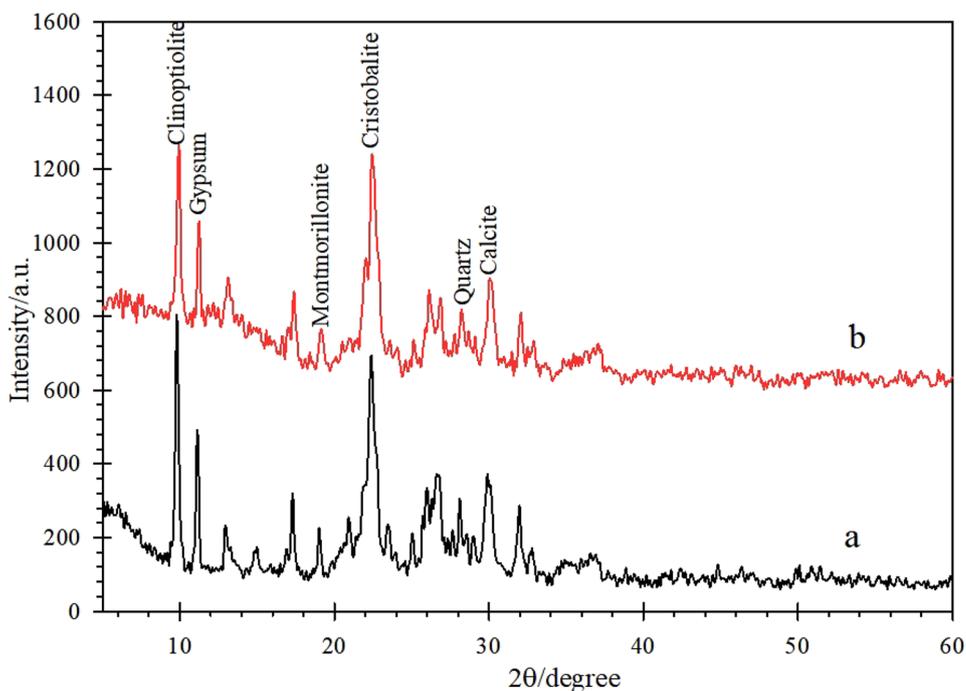
### 3 Results and discussion

#### 3.1 Characterization of modified zeolite by X-ray diffraction analysis

In order to confirm modification of zeolite, the XRD analysis was taken. According to the XRD pattern (Fig. 1) it can be seen that the used zeolite and modified zeolite in this

study were mainly composed of Clinoptilolite, Cristobalite and Gypsum. Calcite, Montmorillonite and Quartz were also found to be low in the zeolite and modified zeolite. As shown in Scheme 1, by modifying the zeolite, Na(I) ion, cationic radius as 95 pm [50], enters into the zeolite framework. By placing Na-form zeolite in a solution containing Fe(III), Na(I) ions replaced by Fe(III) ions (cationic radius as 60 pm) [50] that causes to increasing the cavity size of zeolite [51]. As shown in Fig. 1, the zeolite structure was not changed during the modification and the peak positions for modified zeolite (Fig. 1b) is the same with zeolite (Fig. 1a). Although modification of zeolite by the Na(I) and the Fe(III) ions does not affect the overall structure, but

**Fig. 1** XRD spectra of the **a** zeolite and **b** modified zeolite



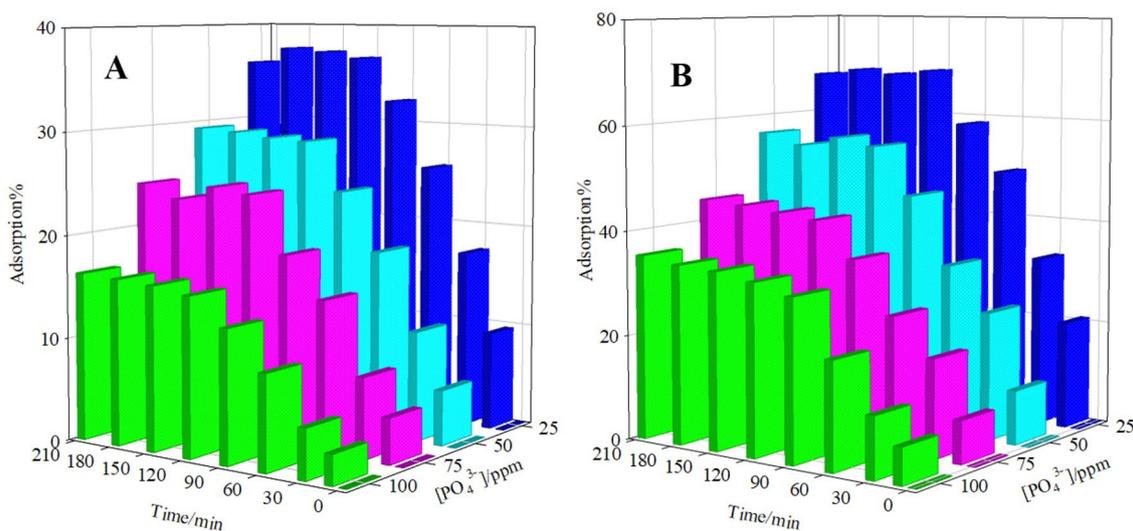
changing the channel size of the zeolite affect on its selectivity. The crystalline structure of modified zeolite is less than zeolite that it can be confirmed by fewer peak heights in the modified zeolite XRD spectrum than zeolite (Fig. 1).

### 3.2 Effect of parameters on phosphate adsorption on the ZCS and the MZCS

Effect of contact time on phosphate adsorption at various initial phosphate concentrations (25.0, 50.0, 75.0 and 100.0 ppm) from solution on the ZCS and the MZCS was investigated (Fig. 2). Results were shown in all phosphate concentrations more than 60% adsorption was achieved in the initial times for both the ZCS and the MZCS. In the initial time, phosphate can be adsorbed on the inner surfaces of deep pores by diffusion into the sorbent matrix through meso- and micro-pores [52]. Adsorption efficiency was reached a maximum value of 32.4% after 150 min for the ZCS and 70.6% after 120 min for the MZCS at the same conditions. One of the main reasons for reducing the maximum adsorption time on the MZCS compared with the ZCS can be attributed to the presence of Na(I) and Fe(III) ions in modified zeolite at the MZCS. By placing these ions in the zeolite framework, it was created an electrostatic field on the inner surface of the zeolite [51] and was increased adsorption capacity and reduced maximum adsorption time of phosphate ion on the MZCS. According to Fig. 2 adsorption efficiency was reduced with an increase in initial phosphate concentration, therefore 25.0 ppm was chosen for other experiments. Adsorption efficiency of the MZCS decreased by increasing phosphate concentration. This phenomenon may be due to this fact that in

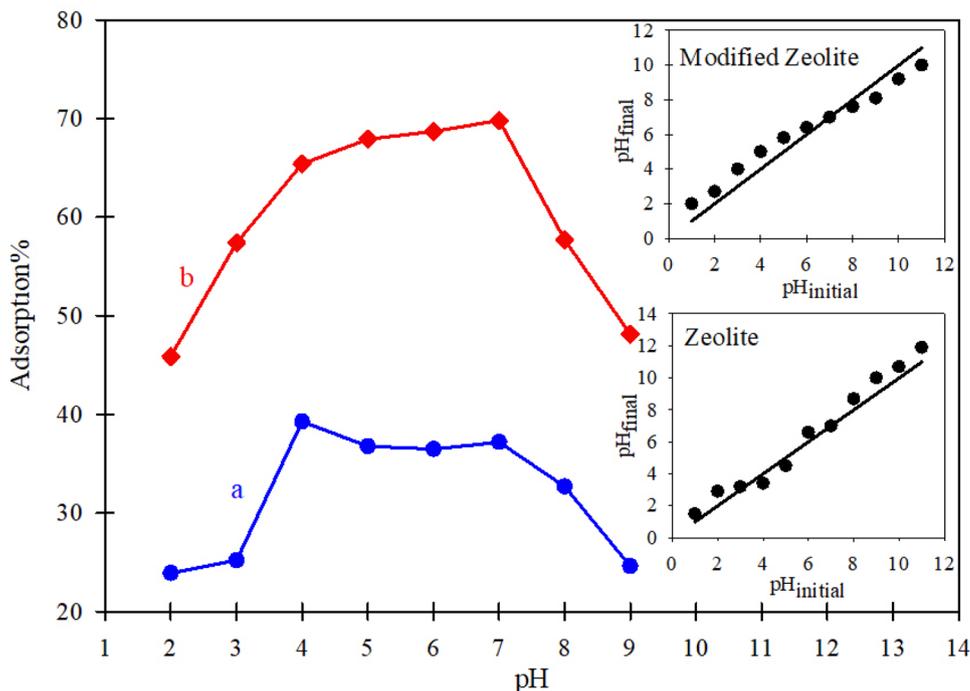
low phosphate concentration the adsorbent site on the surface is high and by increasing the phosphate concentration this active sites filled and a repulsive force due to adsorbed phosphate ions expansion on the surface.

The pH of collecting solution can influence on the surface properties of the adsorbent [53] and therefore strongly affects the mechanism of adsorption on the surface [54]. The point of zero charge ( $pH_{PZC}$ ) was determined using the pH drift method and measuring pH where the zeolite and modified zeolite behave as a neutral species. The  $pH_{PZC}$  was found to be 7.0 for both zeolite and modified zeolite (Fig. 3, Insets). Adsorption phosphate on the ZCS and MZCS at different pH were also investigated to determine the optimum pH. For this object, the ZCS and the MZCS were incubated in separate 25.0 ppm phosphate solution at different pH, then each surface was removed after 120 min and phosphate adsorption of the solution was determined by UV-visible spectrophotometer (Fig. 3). The results were shown that at acidic pH lower than 4.0, phosphate adsorption was come down due to the dealumination of the zeolite at ZCS and MZCS take place and these were lost crystallinity [55]. When the pH increased to 4.0–7.0, changes in the crystallinity was not observed and therefore in this range of pH, the percentage of adsorption for both the ZCS and the MZCS was maximal. Similarly, higher adsorption percentage in this region on zeolite was reported by Nemr et al. [56] and Xiong et al. [57]. In pH above than 7.0, there was competition between  $OH^-$  and phosphate ions in adsorption on the ZCS and the MZCS and according to  $pH_{PZC}$ , repulsion interaction between zeolite and phosphate which led to decrease in phosphate adsorption on both surfaces.



**Fig. 2** Effect of phosphate concentration and contact time on phosphate adsorption on the **a** ZCS and **b** MZCS

**Fig. 3** Effect of collection solution pH on adsorption of phosphate on the (a) ZCS and (b) MZCS. Insets show the  $pH_{PZC}$  curves of zeolite and modified zeolite

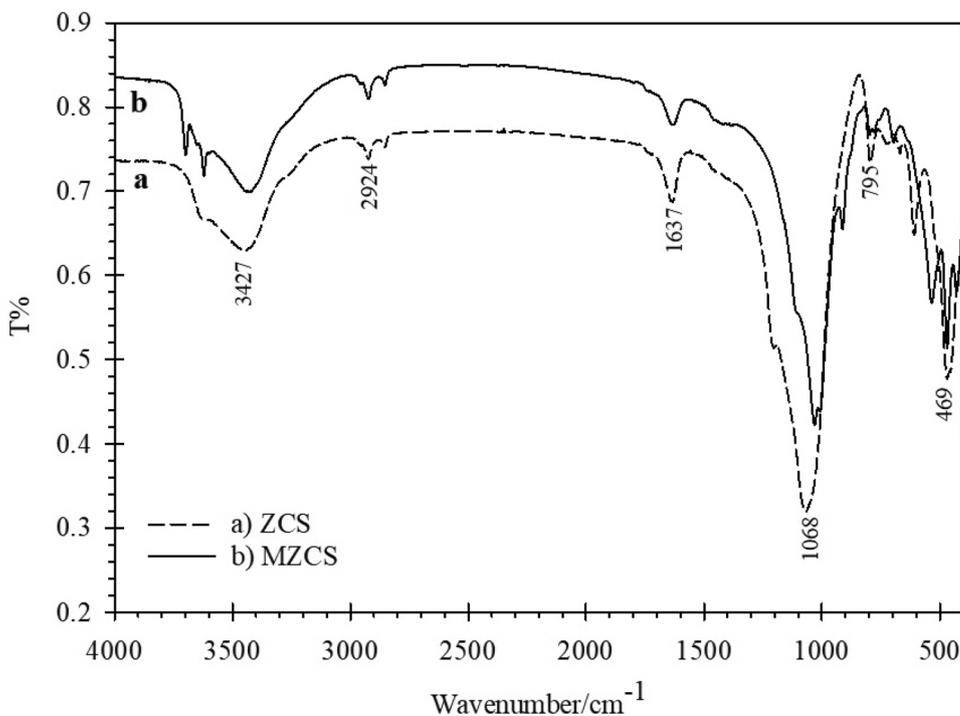


### 3.3 ATR-FTIR analysis

Figure 4 shows the ATR-FTIR spectra for the ZCS and the MZCS. The adsorption band around  $1068\text{ cm}^{-1}$  is attributed to Si–O vibration [58], that the intensity of this band is decreased in the MZCS compared to that in the ZCS. This

is due to the introduction of Fe(III) into the zeolite aluminosilicate framework. The peak at  $795\text{ cm}^{-1}$  corresponds to the stretching vibration of Al–O–Si [59]. A band observed at  $469\text{ cm}^{-1}$  corresponds to Si–O–Si stretching [58, 59] and the bands around  $3424, 2854$  and  $1637\text{ cm}^{-1}$  are attributed to O–H stretching vibration [59, 60]. The peaks assigned to

**Fig. 4** ATR-FTIR spectra of the (a) ZCS and (b) MZCS



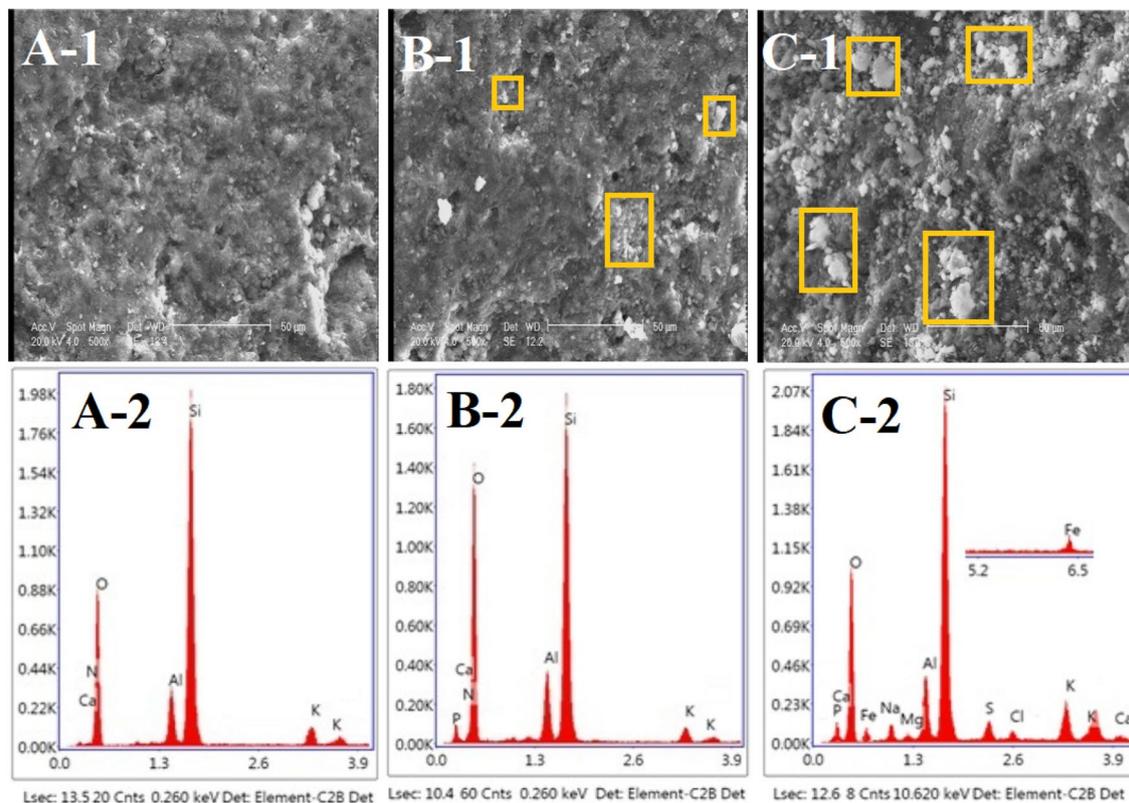
Fe–O and Fe–O–Fe stretching of Fe-zeolite could not be identified which may be due to the characteristic stretching frequency of silicates [61].

### 3.4 SEM and EDX analysis

To evaluate the possibility and comparison of phosphate adsorption by zeolite and modified zeolite, the morphology of zeolite placed zeolite in 25.0 ppm phosphate solution (zeolite-phosphate) and placed modified zeolite in 25.0 ppm phosphate solution (modified zeolite-phosphate) were examined with SEM and EDX (Fig. 5). The SEM images and EDX spectra were supported that phosphate adsorption on zeolite and especially modified zeolite. The white bulky gatherings and P peak in the SEM images and EDX spectra of zeolite-phosphate and modified zeolite-phosphate (Fig. 5B-1, C-1, B-2 and C-2) were demonstrated that phosphate ion was been adsorbed on zeolite and modified zeolite. The higher amount and intensity of that in Fig. 5C-1 and C-2 were confirmed modified zeolite was being successful in adsorbing phosphate ion than zeolite (Fig. 5B-1 and B-2).

### 3.5 Adsorption isotherm of phosphate on the ZCS and the MZCS

To describe the adsorption phosphate isotherm on the ZCS and the MZCS, Langmuir [62–64] and Freundlich [65–67] models were applied and the experimental data were fitted by both models. The values of the correlation coefficient ( $R^2$ ) of linear plots of both models were considered as an evaluation of the best fit [68, 69]. Isotherm parameters are reported in Table 1. The values of  $R^2$  of the Langmuir model were found to be better than that of the Freundlich model for both the ZCS and the MZCS. Table 1 shows the values of  $n$  for both the ZCS and the MZCS are longer than 1 that indicates the adsorption of phosphate at both surfaces is favorable [70, 71]. Compliance experimental data of phosphate adsorption with Langmuir model was suggested that phosphate was adsorbed as a monolayer on both the ZCS and the MZCS [72] and these have equal energy location which each phosphate ion is allocated only to one location, so the distribution of active sites is likely to be adsorbed uniformly and it establishes the strong electrostatic sorbent-adsorbent attraction [73].



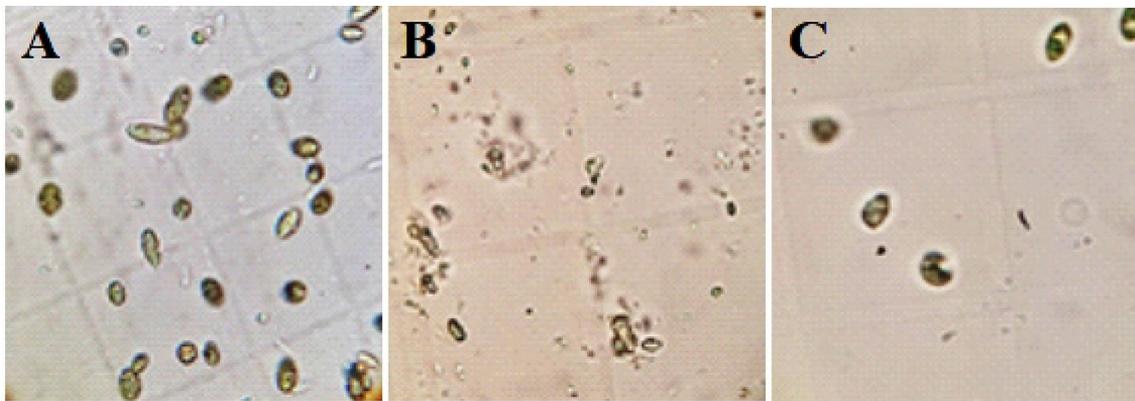
**Fig. 5** SEM image and EDX spectra of the **A-1** and **A-2** zeolite, **B-1** and **B-2** zeolite-phosphate, **C-1** and **C-2** modified zeolite-phosphate. The yellow rectangles show bulky gatherings of phosphate ions

**Table 1** Equilibrium model equations and parameters of the adsorption models fitted to the experimental phosphate adsorption

Surface	Equation	R <sup>2</sup>	q <sub>max</sub> (mg/g)	b (L/mg)
<i>Langmuir model</i>				
ZCS	$\frac{1}{q_e} = 0.158 + 0.723 \frac{1}{C_e}$	0.953	6.317	0.219
MZCS	$\frac{1}{q_e} = 0.141 + 0.441 \frac{1}{C_e}$	0.9724	7.097	0.319
Surface	Equation	R <sup>2</sup>	n	K <sub>f</sub> (mg/g)
<i>Freundlich model</i>				
ZCS	$\ln q_e = 0.379 + 0.421 \ln C_e$	0.898	2.372	1.460
MZCS	$\ln q_e = 0.556 + 0.393 \ln C_e$	0.877	2.546	1.743

Langmuir equation:  $\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}}$ ,  $q_e = (C_i - C_e)V/m$ ,  $q_e$ : amount of adsorbed phosphate per unit mass of adsorbent (zeolite or modified zeolite) at equilibrium (mg/g),  $C_i$ : initial concentration of phosphate in solution (mg/L),  $C_e$ : phosphate concentration at equilibrium (mg/L),  $V$ : volume of phosphate solution (L) taken,  $m$ : mass of adsorbent used (g),  $q_{max}$ : maximum adsorption capacity (mg/g),  $b$ : Langmuir adsorption constant (L/mg)

Freundlich equation:  $q_e = K_f C_e^{(1/n)}$ ,  $K_f$ : capacity of adsorption (mg/g),  $n$ : intensity of adsorption

**Fig. 6** The Algae growth rate image in **a** wastewater, **b** wastewater containing the ZCS and **c** wastewater containing the MZCS

### 3.6 Application for wastewater treatment

The ability of the ZCS and the MZCS for phosphate adsorption and its effect on the growth rate of algae from Isfahan Shahin-Shahr treatment plant wastewater (pH 6.8 and containing 30.0 ppm phosphate) was investigated. The ZCS and MZCS were immersed in 50 mL of wastewater and maintained under suitable physiological conditions (Sect. 2.5). For comparison, 50 mL of wastewater was kept under the same physiological condition. After 30 days, the surfaces were removed from solutions, and the growth of algae in wastewater was investigated. Algae were imaged in three culture media: (a) wastewater, (b) wastewater containing the ZCS and (c) wastewater containing the MZCS (Fig. 6). The number of algae cells per mL of wastewater was counted in each of the three culture media (Table 2). The algae investigating showed that the observed algae were likely to be *Chlorella*. The results of one-way ANOVA with a 95%

**Table 2** Algae cell number in culture medium (A) wastewater, (B) wastewater containing the ZCS and (C) wastewater containing the MZCS

Culture medium	A	B	C
Algae cell number $\times 10^3$ (cell/mL)	3430.7 $\pm$ 10.3	93.4 $\pm$ 5.6	13.2 $\pm$ 1.8

confidence level showed significant differences between B and C with A culture medium ( $P < 0.05$ ), while there was no significant difference between B with C culture medium ( $P > 0.05$ ). According to Fig. 6a and Table 2, the wastewater culture medium has the highest algae content due to the nutrient content of phosphate needed for the growth of microorganisms. By placing the ZCS and the MZCS in the wastewater, due to the adsorption of phosphate ions by them, the growth of algae is reduced (Fig. 6b, c and Table 2). Considering that any micro-algae requires a certain amount of phosphate,

these results indicate that the ZCS and the MZCS can deliver phosphate in wastewater below the limit for algae growth.

## 4 Conclusion

The selective and suitable surfaces were developed based on zeolite and modified zeolite and examined for adsorption of phosphate in aqueous solution. The capability of the surfaces for adsorption of phosphate was established by XRD, SEM–EDX, ATR–FTIR and UV–visible. The Langmuir isotherm gave the best fit to equilibrium experimental data. The merit of the method of modification includes simple fabrication, low cost, good adsorption efficiency, easy to use, no need for electrical and mechanical power. The validity of the method and applicability of the surface were successfully tested by the removal of phosphate and reducing the algae growth rate in treatment plant wastewater.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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