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EVALUATING OF EFFECTIVENESS OF A NATURAL AND MODIFIED SURFACE MEXICAN CLINOPTILOLITE-RICH TUFF IN REMOVING PHENOL AND *p*-NITROPHENOL FROM AQUEOUS SOLUTIONS

Removal of phenol (Phen) and *p*-nitrophenol (*p*-NPhen) from aqueous solutions onto sodium modified (ZG-Na) and surface modified (ZG-HDTMA) natural zeolite has been investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) technique characterizations show that clinoptilolite is the major phase in zeolitic rock. Batch system was considered to determine the kinetics and isotherm type of the adsorption of NO₃ by the ZG-Na and ZG-HDTMA. Results suggest a better fit to the adsorption data than the pseudo-first order kinetic model. It seems that the Langmuir model best describes the experimental data. *p*-NPhen is selectively adsorbed by both ZG-HDTMA and ZG-Na.

1. INTRODUCTION

Phenols belong to a class of organic compounds with aromatic functional groups, being similar in structure to more common herbicides and insecticides which resist biodegradation. In the presence of chlorine in drinking water, phenols form chlorophenol, which has an objectionable medicinal taste [1]. The main sources of phenols are wastewaters of chemical and allied industries. However, it is an important raw material and product of the coking plants and pesticides industries [2]. The USEPA reported phenol in their 1993 Toxic Release Inventory as one of the top twenty five chemicals most discharged by the US industries [3]. Phenols are considered high priority pollutants since they are harmful to organisms at low concentrations and many of

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them have been classified as hazardous pollutants because of their potential harm to both humans and animals. The effects of phenol in humans are similar to those produced in animals. Systemic absorption causes central nervous system impairment, liver and kidney damage, difficulty in swallowing, anorexia, headache, fainting, dark urine and other mental disturbances [4]. Phenols are listed on many target regulatory lists as contaminants of primary interest. The US Environmental Protection Agency (EPA) had instituted a regulation for lowering phenol content in the wastewater to less than 1.0 mg/dm^3 [5].

Several techniques have been proposed in the literature for the removal of organic compounds from solution, such as destructive process including oxidation with ozone [6], hydrogen peroxide [7] or manganese oxides [8] and recuperative processes such as biological treatment [9], membrane separation [10] and solvent extraction [11]. Among the proposed methods, the removal of phenols by adsorption technologies is regarded as one of the best methods because adsorption does not require high operation temperature, the operation procedure being relatively simple [12].

Diverse adsorbent solids have been used to remove phenolic compounds from wastewater such as activated carbon [13, 14] silica [15] polymeric resins [16] fly ash [17] and kaolinite [18].

The use of activated carbon is limited due to cost-effectiveness and difficult regeneration for reuse [19]. There are other interesting alternatives from a cost point of view. Zeolites are very attractive options for the removal of pollutant compounds from water due to the low cost, high availability, high specific surface areas and high cation exchange capacities [20].

Various researchers reported the use of natural and surfactant-modified zeolites to remove organic compounds [21, 22] including phenol derivatives from wastewater [20–26]. However, no investigations reported a comparison between the removal efficiency of phenolic compounds from aqueous solutions and unmodified or modified natural zeolites. Therefore, the aim of this paper was to evaluate the effectiveness of unmodified and modified Mexican clinoptilolite for Phen and *p*-NPhen removal from aqueous solutions. The adsorption kinetics, equilibrium adsorption, and adsorption mechanism were also investigated.

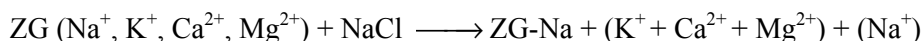
2. EXPERIMENTAL PROCEDURES

Materials. The starting material used in this study was clinoptilolite-rich tuff obtained from natural deposit situated in the state of Guerrero, Mexico. The zeolite was crushed and the grain size was selected between 20 and 30 mesh. Prior to modification, the zeolite was washed with distilled water at $18 \text{ }^\circ\text{C}$ for 6 h to remove suspended materials; the solids were then dried in an electric oven at $60 \text{ }^\circ\text{C}$ for 12 h. This zeolitic sample is referred as ZG.

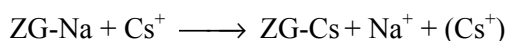
Determination of cation exchange capacity. In order to determine the total cation exchange capacity (CEC) in the zeolite, sodium cations which neutralize the framework of aluminosilicates are exchanged with another cation of a similar size. In contrast, the external cation exchange capacity (ECEC) of zeolite was done by exchanging the sodium cation with the larger cation of surfactant, i.e. HDTMA that could hardly penetrate into the pore of zeolite.

Total cation exchange capacity (CEC). The procedure for the determination of CEC was based on Ming procedure [27]. For the preliminary step, 1 g of ZG was weighed and transferred to a 100 cm³ flask. 50 cm³ of 1 M sodium chloride was added to the sample and the flask was closed tightly. Then the flask was shaken with a mechanical shaker for 1 h at ambient temperature. The supernatant was decanted and this procedure was repeated four more times with a fresh NaCl solution to ensure complete Na-saturation of exchange sites. Subsequently, the sample was washed several times with deionized water until no chloride ions were detected in the washing solution, as was confirmed by the silver nitrate test.

This experimental procedure is summarized by the following chemical equation:



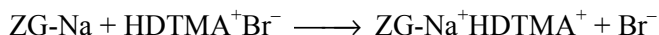
The final step was the addition of 50 cm³ of 1 M cesium chloride into the sample in the flask closed tightly, and shaken with a mechanical shaker for 1 h at ambient temperature. The supernatant was kept in a 250 cm³ volumetric flask. The procedure was repeated four times. The combined solution was diluted to the 250 cm³ mark with deionized water. The sodium concentration was analyzed by the atomic absorption spectroscopy (AAS). This step can be illustrated by the following reactions:



The CEC of the clinoptilolite was calculated by the quantity of Na⁺ removed per gram from the zeolite rock and expressed in meq/g. Sodium was determined in the solutions by AAS. This amount was 78 meq/100 g.

External cation exchange capacity (ECEC). The procedure for ECEC was adopted from Ming et al. [27]. The procedure for ECEC being similar to CEC, differs in the last step in which the sodium is replaced by HDTMA cation. The procedure of determination of ECEC involved: (1) saturation of the sample with sodium cations, (2) exchange the sodium by HDTMA and (3) analyzing the concentration of sodium using AA spectrometry. The last involved the exchange of sodium cations with hexadecyltrimethylammonium cations. The HDTMA solution, 0.25 mmol/dm³ (50 cm³) was added to 1 g of the sample from the previous step. The flask was then closed tightly,

shaken with a mechanical shaker for 8 h at 30 °C. Liquid was decanted into a volumetric flask (250 cm³). This procedure was repeated four times. The combined solution was diluted to the 250 cm³ mark with deionized water. The concentration of displaced sodium was then determined by the AAS. This procedure can be described by the reaction:



The quantity of alkylammonium ions adsorbed on the zeolite was calculated from Na⁺ analysis by AA technique. The ECEC of the clinoptilolite, determined by adsorption of the alkylammonium ions, is 17 meq/100 g.

Preparation of sodium-modified zeolite. The ZG zeolite sample was mixed with an excess of sodium chloride solution (1.0 M) in a 100 cm³ flask. The mixture was shaken in a mechanical shaker for 1 h at ambient temperature. The supernatant was decanted and this procedure was repeated four more times with a fresh NaCl solution to ensure complete Na-saturation of exchange sites. Then, the sample was washed several times with deionized water until no chloride ions were detected in the washing solution (as was confirmed by the silver nitrate test). The Na-saturated zeolitic material was dried at 60 °C for 12 h. The sample obtained from this process is referred as ZG-Na.

Preparation of surfactant-modified zeolite. Surfactant-modified zeolite (ZG-HDTMA) was prepared by reacting ZG-Na zeolite with aqueous solution containing hexadecyltrimethylammonium bromide (HDTMABr, Aldrich). HDTMA was added in an amount corresponding to 100% of ECEC of zeolite. The effect of HDTMA onto zeolite in the adsorption of Phen and *p*-NPhen in water has been studied. The preparation of ZG-HDTMA needed 0.619 g of HDTMA-Br to saturate 100% of the ECEC ZG-Na zeolite (10 g). The data for calculation of the amount of HDTMA needed is as follows: ECEC of zeolite – 17 meq/100 g, molecular weight of HDTMA-bromide – 364.46 g/mol. For 1 meq/100 g = 6.02×10^{20} adsorption sites = 1 mmol/100 g = 1.0×10^{-5} mol/g. Hence, to 1 g of ZG-Na with ECEC = 17 meq/100 g corresponds 1.7×10^{-4} mol of cations. The amount of HDTMA bromide needed is $1 \times 10 \text{ g} \times 1.7 \times 10^{-4} \times 364.46 \text{ g/mol} = 0.619 \text{ g}$ HDTMA-Br.

After the aqueous solution was mixed with zeolite, the mixture was stirred at 30 °C for 24 h in a thermostatic bath. The mixture was then filtered by vacuum filtration, rinsed with deionized water and the solid was dried for 12 h. The resultant ZG-HDTMA was readily used for the adsorption study.

Characterization methods. The characterization of the zeolite has to provide information about structure and morphology. In this study, the phase identifications

within the natural zeolite tuff were determined using X-ray diffraction (XRD) method with a Siemens D5000 diffractometer. XRD patterns were recorded with a CuK_α radiation at $\lambda = 1.5418 \text{ \AA}$ at 40 Kv and 20 mA in the range of 2θ from 2° to 70° , with the scanning speed of 0.1 deg/min. The measured pattern was compared to an existing one.

The scanning electron microscopy (SEM) was used to determine the morphological and qualitative characteristics of the clinoptilolite rich tuff, and electron dispersive X-ray (EDX) analysis was performed on a Philips XL 30, equipped with an Oxford/Link System electron probe microanalyser (EPMA). The images were taken using the magnification of $1500\times$, current intensity of 1000 pA, voltage of 20 kV and the work distance of 25 mm.

Kinetic study. The kinetic study which based on the effect of stirring time for the Phen and *p*-NPhen removal was carried out for the ZG-Na and ZG-HDTMA via the batch method and with various contact times. The stock of each solution of 250 cm^3 of Phen (100 mg/dm^3) and 250 cm^3 of *p*-NPhen (100 mg/dm^3) were prepared by dissolving an appropriate amount of Phen and *p*-NPhen in 250 cm^3 distilled deionized water. A constant amount of zeolite (0.2 g) was mixed with 10 cm^3 solution of Phen or *p*-NPhen in a 15 cm^3 centrifuge tube at pH around 6 in oxidizing conditions. The suspensions were shaken for varying time from 30 min to 15 h, using an orbital shaker with a constant agitation rate and at room temperature. At the end of each time, the phases were separated by centrifugation for 2 min at 1500 rpm. The concentrations of Phen and *p*-NPhen in the supernatant solution after adsorption were determined with the ultraviolet-visible (UV-Vis) spectrophotometer technique. The maximum absorbances wavelength used were 269 nm, and 320.5 nm for phenol, and *p*-nitrophenol, respectively. The calibration plot of absorbance versus concentration for Phen and *p*-NPhen showed a linear working range up to 100 mg/dm^3 with the correlation coefficient ≥ 0.99 . Therefore, the supernatant solutions obtained after adsorption were also analyzed using the same wavelengths. It is important to mention that the adsorption experiments were repeated twice in order to reduce measurement errors. No control of the pH during the sorption processes was considered.

Isotherm study. The adsorption isotherm study was carried out by the batch method for ZG-Na and ZG-HDTMA zeolites. For the purpose of acquiring the value of the maximum adsorption capacity of Phen and *p*-NPhen by surfactant modified zeolite and unmodified zeolite, the isotherm study was carried out with adsorption at various initial concentration of Phen and *p*-NPhen. Basically, 10 cm^3 of solution containing Phen or *p*-NPhen with an initial concentration ranging from 100 to 500 mg/dm^3 (pH around 6) was mixed with 0.2 g of samples in a 15 cm^3 centrifuge tube. The tubes were sealed and shaken for 15 h (this time was obtained from the results of the kinetic studies) at room temperature. Finally, the solutions were centrifuged for

2 min at 1500 rpm. The pH of the solution before and after shaking was not controlled. The concentration of the remaining Phen and *p*-NPhen in the solutions after contact with the samples was determined using UV-Vis technique. The Freundlich and Langmuir isotherms were then used to analyze the results in describing adsorption behaviour of phenol and *p*-nitrophenol on ZG-Na and ZG-HDTMA zeolites.

3. RESULTS AND DISCUSSION

3.1. XRD ANALYSIS

The X-ray diffraction pattern of the natural zeolite tuff is shown in Fig. 1. This diffractogram reveals that the main crystalline phases correspond to clinoptilolite. The maximum reflexions at $2\theta = 9.92^\circ$, 22.43° , and 30.50° correspond to Ca-clinoptilolite (JCPDS 01-083-1261). Other minor mineral components are also observed and identified at $2\theta = 25.8^\circ$ and at 20.8° , which correspond to mordenite and quartz (JPCDS 33-1161) phases respectively. Both phases are associated to the zeolitic rock.

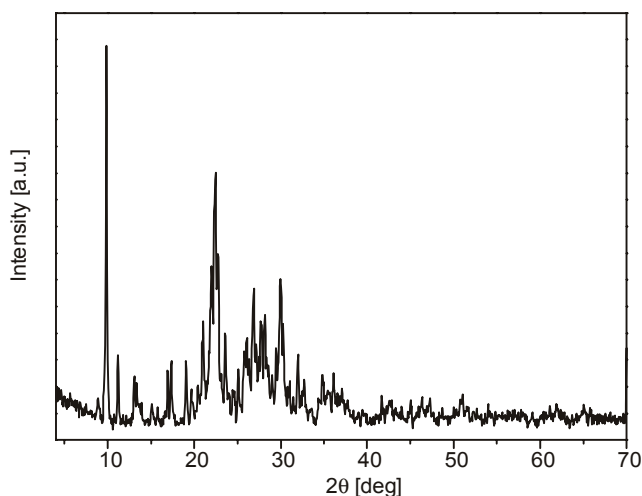


Fig. 1. X-ray diffraction pattern of natural ZG zeolite

3.2. SEM ANALYSIS

The results of SEM analysis confirm those obtained in XRD pattern of the natural zeolite. Two phases were observed by SEM; the crystals of clinoptilolite that showed coffin and cubic-like which exhibit characteristic monoclinic symmetry (Fig. 2a) and a second mineral phase which was identified as a mordenite which occurred as fibres

(Fig. 2b). It was noted that the samples treated with NaCl solution did not show any surface and morphology differences with respect to the natural zeolite tuffs.

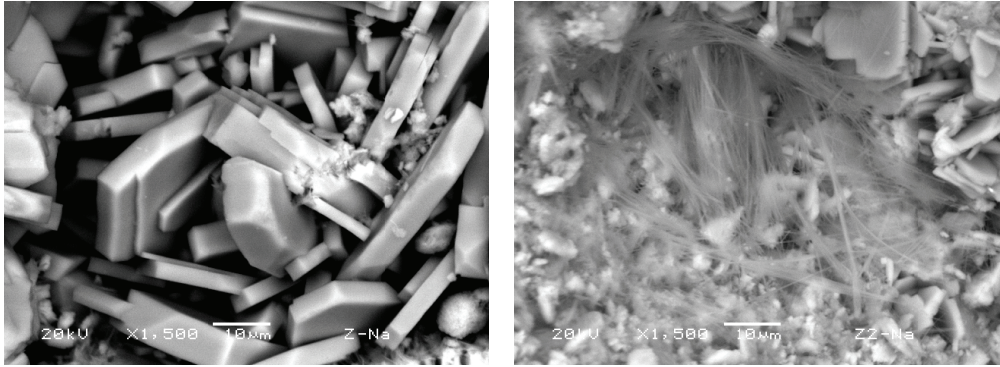


Fig. 2. SEM images of ZG showing the crystalline structures of clinoptilolite (left, 1500 \times) and mordenite (right, 1500 \times)

Chemical composition of the natural clinoptilolite-rich tuff and its sodium form was determined by the EDX analysis. The weight percentage of the sodium and ratio Si/Al increased after the treatment with NaCl solutions as it was expected (Table 1). Experimental data of ratios Si/Al are similar to that obtained by Chmielewska et al., and Arcoya et al. [28, 29].

Table 1

Chemical surface composition of the natural and treated zeolitic mineral determined by EDX analysis [wt. %]

Element	O	Na	Mg	Al	Si	K	Ca	Fe	Si/Al
ZG	49.94	0.11	0.89	7.53	35.74	1.75	3.36	0.68	4.74
Z-Na	49.00	0.63	0.91	6.62	36.44	2.15	3.34	0.91	5.50

3.3. ADSORPTION KINETIC STUDY OF PHENOL AND *p*-NITROPHENOL

In order to accomplish the kinetic study, the contact time experiments of Phen and *p*-NPhen removal by the ZG-Na and ZG-HDTMA zeolites were carried out. The initial concentrations of Phen and *p*-NPhen were 100 mg/dm³, the contact times varied from 30 min to 15 h. The Phen and *p*-NPhen uptake, q (mg Phen or *p*-NPhen adsorbed/g zeolite) was calculated from the equation:

$$q = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 is the initial concentration (mg/dm^3), C_t is the final concentration at time t (mg/dm^3), W is the weight of the adsorbent (g) and V is the volume of the solution (cm^3). The uptake values of Phen and p -NPhen from the solution as a function of contact time are presented in Fig. 3.

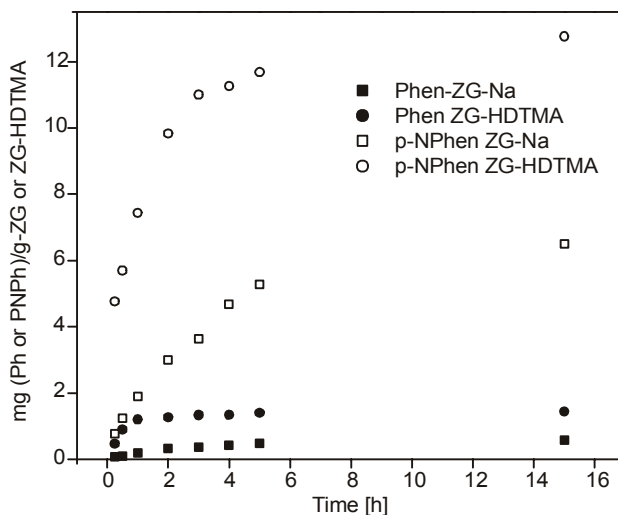


Fig. 3. Effect of contact time on the removal of Phen and p -NPhen on ZG-Na and ZG-HDTMA

As shown in the figure, the removal of Phen and p -NPhen is basically carried in two-stages: i) rapid initial adsorption between 0 and 1 h and between 0 and 5 h for Phen and p -NPhen respectively, ii) slow adsorption where no further significant increase is observed up 1 h for Phen and up 5 h for p -NPhen, independent of the zeolitic material used as adsorbent (ZG-Na or ZG-HDTMA). This trend emphasizes that adsorption times have important effects on the removal efficiency, which increases significantly with increasing zeolite contact time with the Phen and p -NPhen solutions. On the other hand, the time for the adsorption of Phen by unmodified and modified zeolite to reach the equilibrium state was shorter than for p -NPhen. This behaviour can be explained by the properties of the phenolic compounds, where the larger size of p -NPhen molecule needed more time to be adsorbed in the surface the zeolite.

As shown in Figure 3, it is clearly observed that unmodified zeolite have little affinity for Phen and p -NPhen, in contrast, the ZG-HDTMA shows significant adsorption of Phen and p -NPhen from aqueous solution. The ability of the ZG-HDTMA to adsorb Phen and p -NPhen is due to the anion exchange at the positive sites resulting from the HDTMA layer onto the zeolite surface. Furthermore, p -NPhen was found to adsorb more than Phen (reaching the values from 6.5 to 12.76 mg/g for p -NPhen and from 0.58 to 1.44 mg/g for Phen). This can be explained by the lower solubility of

p-NPhen in aqueous solution. The solubility of Phen and *p*-NPhen are 9.3 and 1.4 g/100 g H₂O at 20 °C. A decrease in solubility is associated to an increase in adsorption capacity. Low solubility implies that weak forces exist between solvent and sorbate molecules as a result; high amount of uptake took place. Similar results were obtained by other workers [24, 30, 31]. Denizli stated that the difference in adsorption behaviour of phenol, 2-nitrophenol and *p*-nitrophenol might be due to the different affinities of the three phenolic species for the reactive functional groups [30]. The adsorption capacity for phenol was found to be slightly higher than that of 2-nitrophenol, and this shows that solubility is not all important in this system because if solubility was to be the controlling factor then 2-nitrophenol would have had a higher adsorption affinity than phenol because of its lower solubility in water with respect to phenol.

Mathematical models that are used most frequently to describe kinetics of sorption in a suspension in an agitated batch system are pseudo-first and pseudo-second order equations [32] Equations (2) and (3) are for pseudo-first and pseudo-second order respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} = \frac{1}{h} + \frac{t}{q_e} \quad (3)$$

A plot of $\ln(q_e - q_t)$ against t will give a straight line if the adsorption follows the first order kinetic equation. If the adsorption follows the second order equation, a plot of t/q_t against t will yield a straight line. Therefore, the rate constant and the amount of Phen and *p*-NPhen at the equilibrium can be determined, when fitting the experimental data to Eqs. (2) and (3). The values of the rate constants and amounts of Phen and *p*-NPhen adsorbed on the modified and unmodified zeolites at the equilibrium together with the correlation coefficients for the adsorption of phenolic compounds on ZG-Na and ZG-HDTMA are listed in Table 2. As a result, the adsorption of Phen and *p*-NPhen by the modified and unmodified surface zeolites fitted well with the pseudo-second order model since the correlation coefficient (r^2) was higher than 0.99.

The pseudo-second order adsorption constant (k_2) was four-fold higher when Phen was adsorbed to ZG-Na instead of ZG-HDMTA and was 1.2-folds higher for *p*-NPhen adsorption. This result indicates that ZG-HDTMA influenced the Phen adsorption rate, but not the *p*-NPhen adsorption rate. The k_2 constants were different for Phen and *p*-NPhen. The k_2 constant was 25 times higher for Phen than *p*-NPhen adsorption by ZG-Na and was 7 times higher for adsorption by ZG-HDMTA. According to the pseudo-second order model, maximum adsorption of Phen and *p*-NPhen by ZG-Na and ZG-HDTMA at equilibrium (q_e) depend on both HDTMA adsorbed to the zeolitic

material and the phenolic compound. The best adsorbent was ZG-HDTMA, which adsorbed 8.6 times more *p*-NPhen than Phen (Table 2).

Table 2

Parameters of the pseudo-first and pseudo-second order models for the adsorption of Phen and *p*-NPhen by ZG-Na and ZG-HDTMA zeolites

Phenolic compound	Adsorbent	Pseudo-first order model			Pseudo-second order model			
		k_1 [dm ³ ·h ⁻¹]	q_e [mg·g ⁻¹]	r^2	k_2 [g·mg ⁻¹ ·h ⁻¹]	q_e [mg·g ⁻¹]	h [mg·g ⁻¹ ·h ⁻¹]	r^2
Phen	ZG-Na	0.50	0.34	0.97	2.81	0.53	0.79	0.99
	ZG-HDTMA	0.49	1.23	0.94	0.67	1.59	1,69	0.99
<i>p</i> -NPhen	ZG-Na	0.29	4.43	0.95	0.11	6.67	4,76	0.99
	ZG-HDTMA	0.43	9.12	0.99	0.09	13.69	17,54	0.99

3.4. ISOTHERM STUDY OF PHENOL AND P-NITROPHENOL

The adsorption capacity of the ZG-Na and ZG-HDTMA zeolites for the Phen and *p*-NPhen removal was determined through the adsorption isotherm studies. The isotherm graph for the adsorption of Phen and *p*-NPhen by unmodified and modified zeolite is given in Figure 4. In order to get the information regarding the adsorption capacity of Phen and *p*-NPhen by each sorbents, the Langmuir and Freundlich isotherm adsorption models were used. The results of theoretical calculations for these models are presented by the linear forms of Eqs. (4) and (5), respectively. The values of the parameters of sotherm models are given in Table 3

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e q_m} \quad (4)$$

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (5)$$

where: q_e is the amount adsorbed at the equilibrium [mg·g⁻¹], K_L is the Langmuir constant related to the affinity of the binding site, C_e is the equilibrium concentration of the adsorbate in the solution [mg·cm⁻³], q_m is the maximum amount of solute adsorbed [mg·g⁻¹], K_f and n are the empirical Freundlich constants that are associated with the adsorption capacity and the adsorption intensity, respectively.

When $1/q_e$ is plotted against $1/C_e$, a straight line is obtained with the slope $1/(K_L q_m)$ and the intercept is $1/q_m$.

The adsorption of Phen and *p*-NPhen by ZG-Na and ZG-HDTMA fitted very well with the Langmuir isotherm model because a straight line is obtained when these data

are plotted according to Eq. (5) with the coefficient of determination (r^2) for each set of the linear data exceeding 0.96 as shown in Table 3.

Table 3

Parameters which describe the adsorption isotherms of the phenolic compounds by zeolitic materials

Phenolic compound	Adsorbent	Isotherm					
		Langmuir			Freundlich		
		K_L [dm ³ ·mg ⁻¹]	q_m [mg·g ⁻¹]	r^2	K_f [mg·g ⁻¹]	$1/n$	r^2
Phen	ZG-Na	0.094	0.65	0.97	0.47	0.049	0.91
	ZG-HDTMA	0.007	10.57	0.98	0.41	0.502	0.95
<i>p</i> -NPhen	ZG-Na	0.081	9.02	0.98	4.85	0.098	0.85
	ZG-HDTMA	0.082	15.79	0.97	6.23	0.154	0.82

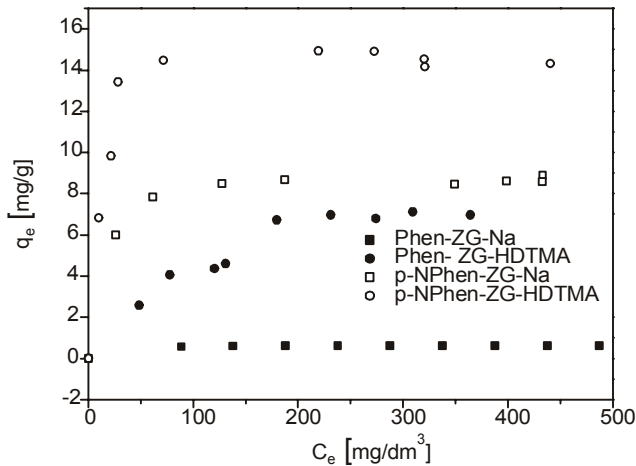


Fig. 4. Adsorption isotherms of Phenol and *p*-nitrophenol on ZG-Na and ZG-HDTMA zeolites

Figure 4 demonstrates that ZG-HDTMA shows higher adsorption of Phen and *p*-NPhen from aqueous solution compared with unmodified zeolite ZG-Na. The adsorption capacity (q_m according to the Langmuir model) of ZG-Na for *p*-NPhen was approximately 14 times higher than for Phen and was around 2 times higher for *p*-NPhen when ZG-HDTMA was used. It is important to note that the HDTMA surfactant improved the adsorption of both Phen and *p*-NPhen (Table 2). The adsorption of Phen or *p*-NPhen to ZG-HDTMA yielded higher K_L values than adsorption on ZG-Na, and K_L parameters were higher for *p*-NPhen adsorption than for Phen adsorption on ZG-Na and ZG-HDTMA.

4. CONCLUSIONS

The Na-saturated form of the Mexican clinoptilolite-rich tuff (ZG-Na) preferentially adsorbed *p*-nitrophenol over phenol. ZG-HDTMA improved phenol adsorption and especially that of *p*-nitrophenol. The equilibrium adsorption and kinetics data were well described by a pseudo-second order and the Langmuir models, respectively. Zeolite surface modification with HDTMA and the properties of phenol and *p*-nitrophenol affected the adsorption process. The adsorption data suggest that Na-saturated and HDTMA-treated Mexican clinoptilolite-rich tuff could be employed as adsorbents for phenol and *p*-nitrophenol removal from water.

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