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Organic dye removal from aqueous media by using acid modified Clinoptilolite

Roya Ebrahimi[1], Afshin Maleki[1,✉], Behzad Shahmoradi[1], Reza Rezaee [1], Hiua Daraei[1], Mahdi Safari[1], Yahya Zandsalimi[1], Pegah Bahmani[1], Shivaraju Harkaranahalli Puttaiah [2]

1. Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran
2. Department of Water and Health, Faculty of Life Sciences, Jagadguru Sri Shivarathreeshwara University, Sri Shivarathreeshwara Nagara, Mysuru-570015, Karnataka, India

ABSTRACT

Dyes are an important class of pollutants which when discharged into water resources can be toxic to the aquatic environment and cause serious problems for public health. Various treatment technologies such as adsorption are in use. For this reason, clinoptilolite was used as a low-cost adsorbent to remove color from aqueous solution. Clinoptilolite was modified with sulfuric and phosphoric acids in order to adsorp aqueous direct red 23. The batch adsorption experiments used dye concentrations ranging from 50 to 200 mg/L. Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), and Fourier transform infrared spectra (FTIR) were used to determine properties of clinoptilolite. To evaluate the experimental data, adsorption isotherms and kinetics were studied. The results showed that experimental data followed both Langmuir and Freundlich isotherms, with a correlation coefficient of 0.95–0.99. Kinetic studies showed that adsorption followed pseudo first-order kinetics. The adsorption results showed that acid-modified clinoptilolite with maximum adsorption capacity of 0.0009 mmol/g was a superior adsorbent compared with unmodified clinoptilolite, according to Langmuir equation. It caused adsorption efficiency in terms of Si/Al ratio 7.5 after 200 min of contact of between 31% to 60%. According to the Dubinin-Radushkevich isotherm model, mean free energy of adsorption (8.2–8.9 kJ/ mol) means that adsorption might follow a weak chemisorption mechanism. We conclude that adsorbing properties of clinoptilolite, a cheap and abundant adsorbent, can be improved and used for removing dyes from wastewater.

Keywords: Adsorption; Clinoptilolite; Direct Red 23; Acid modification

Introduction

In recent decades, increasing environmental pollution has brought about the enactment of regulations for restrictricting effluent discharge.[1] In the last 20 years, the discharge of industrial wastewater containing special pollutants such as dyes into water resources has become an important environmental issue because their toxicity and turbidity levels cause serious problems for human health.[2,3,4] Dye sewage has a complex composition with high chemical oxygen demand (COD), is non biodegradable, toxic, leven carcinogenic and highly colored and consequently, color removal is one of the most important processes in the treatment of this type of wastewater.[2,5,6] About 100,000 dyes are commercially available with a production rate of 7×10^5 tons per year; about 2 percent of these dyes are released into water resources as waste.[7]

Introducing new environmental codes that comply with existing control methods appears to be either impossible or expensive.[8,9,10] In addition, the conventional removal methods have low efficiency. Hence, one of the suitable approaches is to modify available methods and alter their properties.[11,12,13] Clinoptilolite, a natural zeolite, is one of the unique candidates for adsorption of organic pollutants because it has special properties such as suitable structure, high cationic exchange potential, high stability, cost-effectiveness, and is abundantly

✉ *Afshin Maleki*
maleki43@yahoo.com

distributed.[14,15,16] Its excellent ion exchange ability and high surface area are the two special properties that make zeolite a suitable candidate for many environmental applications in the field of pollutants removal.[17,18]

Clinoptilolite belongs to the alkaline earth hydrated aluminosilicates. It has a tetragonal crystalline structure with pores and channels of 3–10 angstroms; the pores contain 10%–20% water. The cationic exchange capacity of 1.16–4.73 meq/g of clinoptiloliteis is attributed to its structure.[19] Many industries increasingly use clinoptilolite as adsorbent because of its molecular structure and properties. Its three main properties—cationic exchange, adsorption, catalytic properties—have resulted in clinoptilolite being applied in environmental issues.[19,20,21] Clinoptilolite has characteristic cavities and channels that make it suitable for selective adsorption of certain ions or molecules in the presence of other species. Its capacity for reversible dehydration and cationic exchange with negligible change in its structure are the most important features of clinoptilolite. However, there is a demand to further increase the adsorption capacity of clinoptilolite with suitable modifiers.[22,23,24] This modification could change the surface chemistry through chemical or thermal activation.[22,25,26] Several researchers have used different methods and chemicals as modifiers to enhance zeolite adsorption capacity.[27] One of the main approaches to increase the adsorption properties of clinoptilolite is chemical activation process using acid. In this process, hydrogen ions are replaced with changeable ions. The formation of these changeable ions creates a porous structure and high specific surface area, which eventually increase adsorption capacity.[25,26] Different concentrations of acid solutions improve the porosity and size distribution of clinoptilolite, depending upon the clinoptilolite nature. This study aimed to alter the structure of clinoptilolite by modifying it with acid and to evaluate the effects of surface modification on the adsorption efficiency of direct red 23 (one of the most frequently used dyes in the textile industry that is toxicity and carcinogenic). SEM, XRF, XRD and FTIR were used to determine physical, chemical, and morphological properties of natural and modified clinoptilolite. The adsorption isotherms and kinetic models were also investigated.

Materials and Methods

Sulfuric and phosphoric acids were used to modify clinoptilolite. Clinoptilolite was purchased from Arand Toosca, Iran. Clinoptilolite was first grounded in order to prepare unmodified adsorbent and then was separated using a graded sieve (ASTM standard seive) to get the size range 0.1 mm. The product was then stirred for 1 h in deionized distilled water to remove any potential impurities from the graded clinoptilolite. Next, the liquid phase was separated using a standard sieve and dried at 70 ºC after washing several times with deionized water. The final clinoptilolite was kept in desiccator. The chemical was modified by adding 10 g clinoptilolite to polyethylene containers and then a certain amount of sulfuric/phosphoric acids (1:10 ratio of mass to volume) with different molar concentrations were added. The solid phase was separated using Millipore and Whatman filters and washed with distilled water. After washing, the acid-modified clinoptilolite was dried at 70 ºC and kept inside the desiccator. The acid-modified clinoptilolite composition was determined using X-ray fluorescence (XRF). Table 1 shows the results of the elemental analysis of unmodified and modified clinoptilolite. The morphological properties of unmodified and modified clinoptilolite were analyzed using scanning electron microscopy (SEM, JEOL, JSM 5800) coupled with energy dispersive X-ray analysis (EDAX) with 20 kV at 2,500 times magnification to compare the effect of pretreatment. The funcational groups were assessed using Fourier transform infrared spectroscopy (FTIR) spectra in KBr pellets using a Tensor 27 spectrophotometer (Bruker Optik GmbH, Germany) in the wave numbers range of 500–4000 cm^{-1}. X-ray analysis of zeolites was performed with a EQUINOX 3000 - Inel, X-Ray diffraction systems using Cu*Kα* radiation (30 kV, 20 mA, k = 1.54059 Å) over the range of 5° < 2θ <60° with step width of

0.03°. Digimizer software version 4.1.1.0 was used to determine the mean diameter and particle size distribution of unmodified and modified clinoptilolite.

Two sulfuric acid and phosphoric acid-modified clinoptilolite groups were prepared and their adsorption efficiency evaluated using direct red 23 (DR 23). From each group, the most efficient clinoptilolite was selected as the best adsorbent and subsequent experiments were conducted using those adsorbents. The operational parameters studied were acid concentration, contact time, solution pH, initial dye concentration, and adsorbent dosage. After each run, the instrument was turned off and after 10 min the solution was centrifuged and the liquid was read using spectrophotometer. These steps were repeated for each adsorbent. Adsorption experiments were conducted in a batch system. In each case, the adsorption capacity was calculated using the following equation.[28,29]

$$Q_t = \frac{V(C_i - C_t)}{m}$$

Where, Q_t is the amount of dye adsorbed per unit mass of adsorbent, C_i is the initial concentration of dye, C_t is the final concentration of dye at the time t, V is the volume of solution, and m is the mass of adsorbent. The effect of the initial DR 23 concentration on the adsorption was evaluated for 7 hr to determine the coefficients of adsorption, kinetics and isotherm constants. The data were analyzed using the equations of Langmuir isotherms, Freundlich, and Dubinin-Radushkevich. The reaction kinetics were evaluated using equations of pseudo first-order and pseudo second-order kinetics. All chemicals used were purchased from Merck, Germany. Each experiment was repeated twice and each container used was pickled and finally washed with deionized distilled water to eliminate any potential contamination.

Results and Discussion

Fig. 1 shows the XRD spectra of unmodified and acid-modified clinoptilolite. The acid-modified clinoptilolite displays identical characteristic peaks as the unmodified zeolites, suggesting that the modified clinoptilolite has kept the crystalline structure of unmodified clinoptilolite after modification with both acids (H_2SO_4 and H_3PO_4).[30] However, relative intensities of the low-angle peaks (53.05, 65.95, and 78.89°) decreased compared with the high-angle peaks, which could be because of the effect of the acids applied on the zeolite surfaces.[31,32] Moreover, a light shift of the peaks in the chemically modified zeolite is more noticeable than with the unmodified zeolite. FTIR spectroscopy studies were used to identify the chemical groups of raw and modified zeolite in order to provide clear evidence for the functionalization of clinoptilolite. Figure 2 shows the FTIR spectra of unmodified and chemically modified clinoptilolite. In the unmodified clinoptilolite, the adsorption bands around 1026 cm^{-1} could be attributed to the stretching vibration of -C-N- bond. Similarly, absorbance bands around at 1645 and 1728 cm^{-1} could be attributed to the stretching frequencies of the C=C bond and C=O bond. Similar peaks and functional groups were observed in the modified clinoptilolite. Actually, modification of clinoptilolite using H_3PO_4 and H_2SO_4 did not result in adding new peaks on the surface of the clinoptilolite modified, indicating purity of zeolite surface and no attachment of functional group on the surface of the clinoptilolite. However, the intensity of the peak at 1026.08 cm^{-1} increased significantly, which could be attributed to the effect of the acids applied. Finally the FTIR results showed that the position, height, and width of each peak are nearly identical for both modified and unmodified samples.[33]

Figure 3 illustrates the dynamic light scattering (DLS) and SEM images of unmodified and chemically modified zeolite. The DLS histograms show that chemically modified zeolites have better normal distribution than unmodified zeolite. From the DLS data it can be concluded that a nearly monodisperse population of the modified zeolite particles is produced with average diameter 70 nm with an indication of a minor population of larger aggregates.[34] Although the particle size did not reduced significantly, the SEM images

show noticeable changes in morphology. On the other hand, the amorphous particles were flake shaped with sharp edges, in the case of H_3PO_4 modified zeolite.
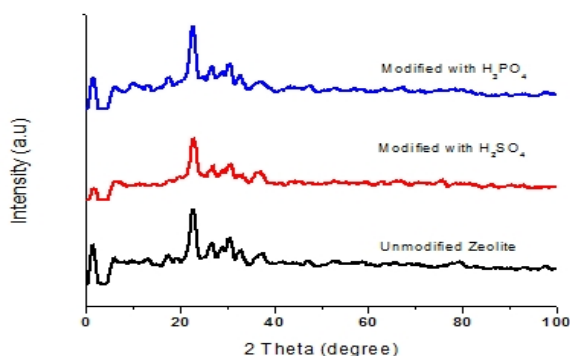

Fig. 1. Powder XRD of unmodified and chemically modified zeolite

Table 1 shows XRF analysis of the unmodified and modified clinoptilolite. The modification was effective in changing the structure of clinoptilolite and the increase of DR 23 adsorption rate could be attributed to the effect of acid modification (Table 1).
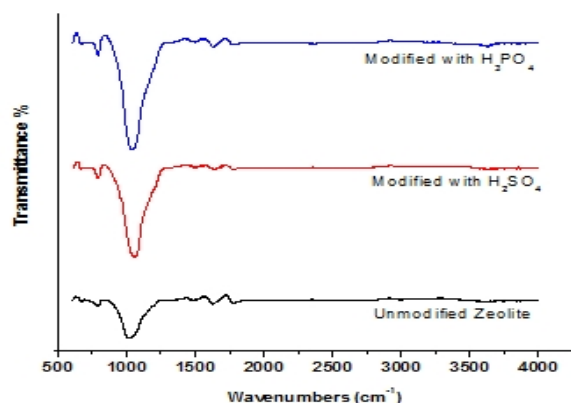

Fig. 2. FTIR spectra of unmodified and acid- modified clinoptilolite

Table 1. XRF analysis of the natural and modified zeolites

Constituents weight (%)	Type of clinoptilolite		
	Raw	Phosphoric acid-modified clinoptilolite	Sulfuric acid-modified clinoptilolite
SiO_2	66.5	67.2	69.5
Al_2O_3	11.8	11	9.2
TiO_2	0.2	0.2	0.18
Fe_2O_3	1.3	1.25	1.15
CaO	3.1	2.8	2.1
MgO	0.7	0.65	0.49
K_2O	3	2	2.3
Na_2O	2	1.1	0.75
P_2O_5	0.01	0.1	0.01
L.O.I.	12	15	16

Clinoptilolite is a natural mineral substance that has many micropores in its crystal structure. Its main mechanism of absorption is ion exchange. In addition, the adsorption process can be carried out through adding functional groups on the zeolite crystal surface. However, studies have shown that clinoptilolite does not have considerable efficiency to adsorp dyes from aqueous media, compared with minerals such as clay. The results of Armagan et al. showed that Turkey natural zeolite had low efficiency in removing three dyes of Everzol black, Everzol red, and Everzol yellow.[35] One common method to increase the efficiency of absorption of mineral substances is acid modification using acids such as sulfuric acid and phosphoric acid. Acid modification of clinoptilolite increases the micropore volume and therefore the adsorption capacity. Nevertheless, in acid modification adding positive functional groups reduces the negative surface charge and increases the hydrophilic properties of the clinoptilolite surface.[35,36] The ratio of silicon to aluminum in the zeolite structure is one of the factors in adsorption efficiency. Acid modification of clinoptilolite results in increasing silicon to aluminum ratio from 5.6 in unmodified clinoptilolite to 6.1 and 7.6 in clinoptilolite modified by sulfuric acid and phosphoric acid, respectively.

Increasing the ratio of silicon to aluminum in the clinoptilolite leads to an increase in adsorbent saturation time. Moreover, it has been confirmed that the ratio of silicon to aluminum in clinoptilolite modified with phosphoric acid is more than with modification using sulfuric acid. In addition, the use of inorganic acids causes the loss of organic impurities from the surface of zeolite and increases surface sites to adsorb the pollutants. Figs. 4 to 6 show the effect of acid modification and changes in initial dye concentration on removal efficiency of clinoptilolite; the plots presented confirm higher efficiency of acid-modified clinoptilolite than with unmodified clinoptilolite. In addition, results show that sulfuric acid-modified clinoptilolite (Figure 6) exhibits higher efficiency than phosphoric acid-modified clinoptilolite (Figure 5) for removal of DR23.

Nevertheless, the results show that increasing initial concentration of dye causes reduction of removal efficiency of clinoptilolite. Increasing the initial concentration of pollutants in the environment could occupy the adsorption sites and limit the rate of adsorption, reducing the adsorption efficiency. On the other hand, the results show that over time, the efficiency of adsorption is increased. Moreover, the efficiency of DR23 adsorption on clinoptilolite was relatively quick in the early stages and then

reduced. In general, the adsorption rate is low and the time to balance takes approximately 200 minutes. Accordingly, the maximum removal efficiency of DR23 with concentrations of 50, 100, 150 and 200 ppm was 9%, 12%, 13%, and 18% for unmodified clinoptilolite (Figure 4), and 20%, 29%, 38%, and 50% for phosphoric acid-modified (Figure 5), and 31%, 38%, 47%, and 60% sulfuric acid-modified clinoptilolite in equilibrium time of 200 minutes.
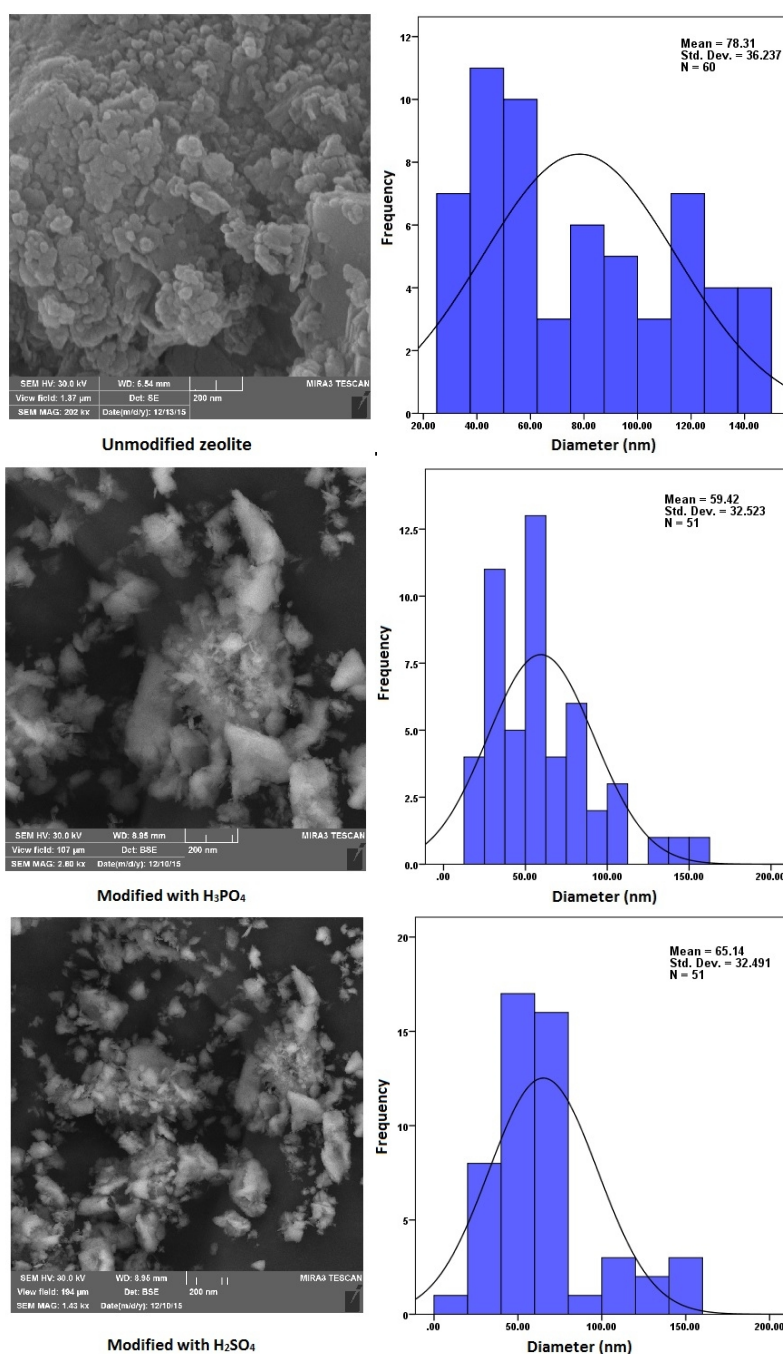

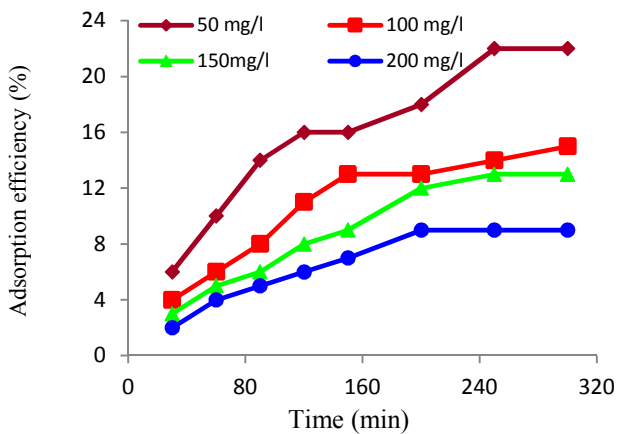Fig. 3. DLS and SEM images of unmodified and chemically modified zeolite

Fig. 4. Effect of initial concentration on adsorption of DR 23 by raw clinoptilolite in various contact time (pH= 4, adsorbent dose= 10 g/l)
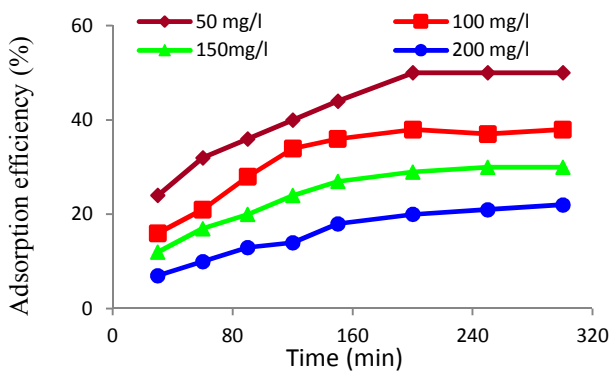

Fig. 5. Effect of initial concentration on adsorption of DR 23 by modified clinoptilolite with phosphoric acid in various contact time (pH= 4, adsorbent dose= 10 g/l)

The effects of initial pH on removal efficiency of DR23 using sulfuric acid and phosphoric acid-modified clinoptilolite are shown in Figure 7. As seen in Figure 7, by increasing pH, the dye removal efficiencies for both acid-modified adsorbents are reduced so that increasing pH from 4 to 9 reduced the dye adsorption efficiency from 52% to 36% and from 61% to 37% for phosphoric and sulfuric acid-modified clinoptilolites, respectively. The pH of environment is one of the main factors in the adsorption process. Changes in pH alter the active sites and effective functional groups on the adsorbent surface. The pH changes can also alter the structure of the substance adsorbed. DR23 belongs to anionic dyes and the presence of sulfonate groups in its structure makes the dye surface negative. The surface charge of clinoptilolite is negative; hence, negatively charged molecules, such as anionic dyes, are

excreted.[37]. Increasing media pH results in increasing negative functional groups such as hydroxyl on the adsorbent surface, which make the surface more negative, thereby, reducing adsorption of the pollutant. In addition, the study results showed that increasing the amount of adsorbent has a direct effect on clinoptilolite efficiency in adsorbing DR23 (data not shown). With the increasing amount of adsorbent surface, adsorption sites and thereby removal efficiency increased. However, when adsorbent dosage increases due to the unsaturated sites, the amount of dye adsorption (mg) per unit weight of adsorbent (g) will often decrease. On the other hand, the whole adsorption sites on the adsorbent are not saturated because of the scarcity of the adsorbate, therefore, the adsorption rate per adsorption unit decreases.[38,39]
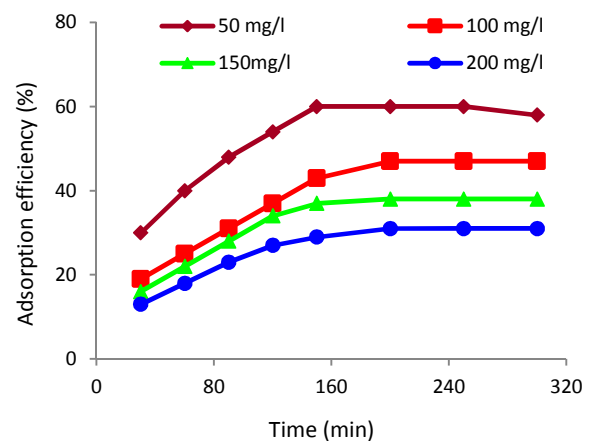

Fig. 6. Effect of initial concentration on adsorption of DR 23 by modified clinoptilolite with sulfuric acid in various contact time (pH= 4, adsorbent dose= 10 g/l)
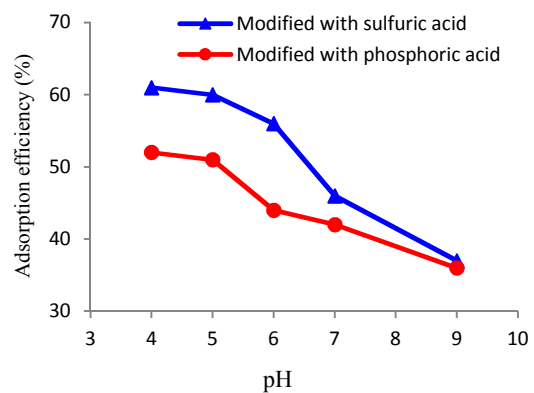

Fig. 7. Effect of pH on adsorption of DR 23 by acid modified clinoptilolites (C_0=50 mg/l, t=200 min, adsorbent dose= 10 g/l)

Adsorption isotherm

One of the important factors in the adsorption process is using the adsorption isotherms. In fact, the behavior of adsorbent and adsorbate is analyzed by adsorption isotherms. In addition, the adsorption capacity of the absorbent and its required optimum value are determined using adsorption isotherm. Table 2 shows Q_L, K_L, K_F and b_F values obtained using linear regression. According to Table 2, the correlation coefficient (R^2) obtained for raw clinoptilolite, sulfuric acid and phosphoric acid-modified clinoptilolite was 0.95, 0.98, 0.99, respectively. The results show that the adsorption isotherm of DR23 using clinoptilolite almost follows the Langmuir model. Nevertheless, the results of this model match with its mathematical equations. Because, in the Langmuir model, the adsorbent surface is considered uniform and equal; hence, the distribution of adsorption sites on the adsorbent surface are identical. Despite Langmuir model, which clearly showed isotherm adsorption process, other isotherms such as Freundlich model and Freundlich coefficient were used to further describe the adsorption process (Table 2). The results of this model showed that like Langmuir, the adsorption of DR23 on the clinoptilolite surface follows this model very well.

Table 2. Parameters of the Langmuir and Freundlich isotherms for adsorption of DR 23 on different type of adsorbents

Type of adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	Q_L (mmol g^{-1})	K_L (L mmol^{-1})	R^2	K_F (mmol g^{-1})	b_F (L g^{-1})	R^2
Raw	0.0003	15.42	0.95	0.0005	0.49	0.95
Modified with phosphoric acid	0.0006	54.5	0.98	0.0009	0.29	0.83
Modified with sulfuric acid	0.0009	26.12	0.99	0.0015	0.38	0.98

The effect of temperature (thermodynamics) on DR23 adsorption process was assessed using the Dubinin-Radushkevich equation and the amount of E achieved was 8-9 KJ/mole. Moreover, the mean adsorption free energy (E), according to Freundlich, and the results of data linear regression for raw clinoptilolite, sulfuric acid and phosphoric acid-modified clinoptilolite achieved was 8.2, 8.6, and 8.9 KJ/mole, respectively. When the value of E is less than 8 KJ/mole, the dominant mechanism in the adsorption process is physical adsorption, while for E values between 8 and 16 KJ/mole, adsorption mechanism is ion exchange chemical process.[28] Therefore, based on the values of E obtained, it can be concluded that the dominant mechanism of adsorption of DR23 using clinoptilolite is weak chemical. To better understand the dynamic and accurate prediction of models, researchers use the adsorption kinetics. Using adsorption kinetics, the amounts of ions adsorbed in the adsorption process is predictable. In this study, the kinetics of pseudo-first and pseudo-second orders were used to describe the data obtained from the process of DR23 adsorption. Table 3 tabulates the adsorption rate constant (K_I), pseudo-first-order kinetics, and Qe obtained from different concentrations of the dyes shown.

Table 3. Pseudo-first-order and pseudo-second-order kinetic parameters for adsorption of DR23 at different initial concentrations

Type of adsorbent	C_0 (mg l^{-1})	Expt. Qe * (mg g^{-1})	Pseudo first order			Pseudo second order		
			Cal. Qe ** (mg g^{-1})	K_I (min^{-1})	R^2	Cal.Qe ** (mg g^{-1})	K_{II} (g mg^{-1} min^{-1})	R^2
Raw	50	0.09	0.1	0.016	0.94	0.16	0.051	0.98
	100	0.15	0.2	0.014	0.94	0.23	0.029	0.93
	150	0.17	0.18	0.009	0.92	0.35	0.012	0.90
	200	0.18	0.17	0.009	0.97	0.30	0.017	0.94
Modified with phosphoric acid	50	0.25	0.19	0.011	0.99	0.30	0.065	0.99
	100	0.38	0.51	0.02	0.97	0.46	0.039	0.99
	150	0.43	0.58	0.019	0.87	0.55	0.026	0.98
	200	0.40	0.45	0.013	0.98	0.61	0.014	0.99
Modified with sulfuric acid	50	0.30	0.24	0.015	0.97	0.42	0.039	0.98
	100	0.47	0.53	0.015	0.93	0.77	0.011	0.97
	150	0.57	0.85	0.023	0.94	0.87	0.013	0.98
	200	0.62	0.73	0.018	0.98	0.96	0.012	0.99

* experimental data

** calculated or estimated from the model

Based on the R^2 values presented in Table 3, it can be concluded that linear regression is an adequate description of the data obtained. However, the calculated Qe for various concentrations of DR23 is much smaller than the Qe obtained from experimental data. Pseudo first-order kinetics is a good way to describe the scientific data but its accuracy to predict Qe is low. Therefore, in this study, the kinetics of pseudo second-order was used for further investigation. The kinetics results indicated that the predicted value Qe is distinct from the Qe value obtained from experimental data. Thus, it can be concluded that compared with pseudo second-order kinetics, the pseudo first-order kinetics presents a better description of the adsorption process of DR23 using clinoptilolite.

Conclusion

The study was conducted at batch scale and the adsorption efficiency of raw and modified clinoptilolite was assessed as cheap adsorbents in adsorption of DR23 in aqueous media. Sulfuric acid and phosphoric acid were used to modify the adsorbent surface and increase the adsorption efficiency. According to the results, efficiency of removing DR23 was higher using modified clinoptilolite rather than raw clinoptilolite. In addition, results showed that the sulfuric acid-modified clinoptilolite had higher efficiency in DR23 adsorption than phosphoric acid-modified clinoptilolite. Nevertheless, time to equilibrium for the modified adsorbent was about 200 minutes. By increasing pH, dye removal for both acid-modified adsorbents declined. The results show that the adsorption isotherm of DR23 on clinoptilolite follows the Langmuir model. Moreover, the pseudo first-order kinetics gives a better description of adsorption process of DR23 than pseudo second-order kinetics. The effect of temperature (thermodynamics) on the DR23 adsorption process was investigated using the Dubinin-Radushkevich equation and the amount of E obtained was 8–9 KJ/mole, indicating the adsorption process might follow a weak chemisorption mechanism.

Conflict of Interests

The authors declare that they have no conflict of interest.

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