

NATURAL AND ACID MODIFIED CLINOPTILOLITE FOR ADSORPTION OF AQUEOUS DIRECT DYE: PARAMETERS, ISOTHERM AND KINETIC

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ABSTRACT

Carcinogenic and mutagenic potential of some azo dyes as a category of common dyes in different types of industries has been reported. So, treating these compounds before entering the environment is essential. Among various removal technologies, adsorption has a particular place for dye removal. Therefore, this research focuses on the removal of direct red 23 dye (RD 23) from aqueous solution using clinoptilolite (natural zeolite) and its acid modified form as a low-cost adsorbent. Sulfuric acid and phosphoric acid were used to improve the adsorption capacity of clinoptilolite. The influence of acid concentration, contact time, solution pH, initial dye concentration and adsorbent mass has been studied. In order to understand the adsorption process, adsorption kinetics and equilibrium isotherms were also studied. Results showed that clinoptilolite has a limited adsorption capacity for dye adsorption but it can be distinctly improved by modifying its surfaces with acid. Experimental results also showed that sulfuric acid have better performance than phosphoric acid for RD 23 adsorption. The best results were obtained in terms of efficiency for modified clinoptilolite with Si/Al ratio 7.5 after 3 h of contact between 30 and 58 percent. Among the models tested, both the Langmuir and Freundlich models represented the experimental data well. It was also found that adsorption of dye by clinoptilolite followed pseudo first-order kinetics. According to the Dubinin–Radushkevich isotherm model, mean free energy of adsorption (11.2-12.9 kJ/ mol) indicates that adsorption might follow a chemisorption mechanism.

Keywords: Clinoptilolite, adsorption isotherm, direct dye, acid modification

1. Introduction

Rapid development of environmental pollution has resulted in enacting restricted regulation for effluent discharging during recent decades. New environmental regulations compliance with existing control methods not only seem impossible but also include huge cost. Moreover, the conventional removal techniques do not have required efficiency; hence, modification of available methods and changing in properties is always considered as a suitable strategy in this regard. Meanwhile, zeolite has attracted considerable attention due to specific spatial structure, high cationic exchange potential, chemical, physical, and thermal stability, cost-effectiveness, abundant distribution throughout the world, and no need for recovery (Chang *et al.*, 2002; Al-Anber and Al-Anber, 2008; Oei *et al.*, 2009).

Zeolite belongs to the alkali metals and alkaline earth hydrated aluminosilicates with tetragonal crystalline structure having pores and channels of 3-10 angstroms. There is 10-20 percent water inside the pores. Having such structure allows zeolite to have cationic exchange capacity of 2.16-4.73 meq/g (Kocaoba *et al.*, 2007). Owing to their molecular structure, application of natural zeolites as adsorbent has been increasingly considered in many industries. Their three main cationic exchange, adsorption, and catalytic properties have resulted in their application in various industrial fields including environmental application (Roque-Malherbe, 2000; Kocaoba *et al.*, 2007; Stylianou *et al.*, 2007). Cavities and channels of zeolite are its characteristics, which cause selective adsorption phenomenon that is absorption of a certain ion or molecule in the presence of other species. The most important feature of zeolites is their capacity in reversible

dehydration and cationic exchange without structural change. This property will change and increase the selectivity of zeolites. Application of unmodified and modified zeolites is growing rapidly in adsorption of cations and anions from contaminated environments (Benkli *et al.*, 2005; Coruh, 2008). Therefore, in order to create new or improve properties, zeolites can be chemically or thermally activated and modified through different methods (Chao *et al.*, 2002; Benkli *et al.*, 2005; Ghobadi *et al.*, 2008). Chemical activation process using acid is the main process used today to promote optimal absorption characteristics. In this process, hydrogen ions are replaced with changeable ions. The formation of these changes lead to the creating porous structure and high specific surface area, which eventually increase the adsorption capacity (Chao *et al.*, 2002; Ghobadi *et al.*, 2008). Depending upon the zeolite's nature, acidic solutions at different concentrations would improve porosity and size distribution of zeolites. Thus, the aim of this study was to alter the structure of Clinobetirolite (one of the most used natural zeolites) and to evaluate the effects of this modification on the dye removal efficiency.

2. Materials and methods

Zeolite used in this study was obtained from Arand Toosca. First, we grounded zeolite in order to prepare unmodified adsorbent and then we separated it using graded sieve (ASTM standard seive) in the size range 0.1 mm. In order to remove impurities from the graded zeolite, it was stirred for 1 h in deionized distilled water; then the liquid phase was separated by standard sieve and then was dried at 70 ° C after several times washing with deionized water and later was kept in desiccator. We added 10 g zeolite to the polyethylene containers for chemical modification and a certain amount of the desired acids (1:10 ratio of mass to volume) with different molar concentrations were added and modified. Then we isolated the solid phase using Millipore and Whatman filters and washed by distilled water (rinsing was continued until pH of the drainage became 7). After washing, the zeolite was dried at 70 ° C and was kept inside the desiccator. In order to determine the properties of the modified zeolite, X-ray fluorescence (XRF) was used and its components were determined. The results of the chemical composition of raw and modified zeolites are presented in Table 1.

All of zeolites were divided into two sulfuric acid and phosphoric acid-modified zeolite groups and the decolourization efficiency was tested using direct red 23 (DR 23). The most efficient zeolite of each group was selected as the best adsorbent and the other experiments were conducted using these adsorbents.

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 ₂ O ₃	11.8	11	9.2
TiO ₂	0.2	0.2	0.18
Fe ₂ O ₃	1.3	1.25	1.15
CaO	3.1	2.8	2.1
MgO	0.7	0.65	0.49
K ₂ O	3	2	2.3
Na ₂ O	2	1.1	0.75
P ₂ O ₅	0.01	0.1	0.01
L.O.I.	12	15	16

To determine the effects of pH and optimum pH, experiments at different pH (4, 5, 6, 7 and 9) with a constant concentration of dye (100 mg/l) were performed. To induce mixing and contact between the absorbent and dye solution, we used Jar instrument (speed = 100 rpm). After each run, the instrument was turned off and after 10 minutes, the solution was filtered by Whatman filter paper and, after centrifugation, the liquid resulted was prepared to determine the efficiency. This was repeated for the other adsorbents.

Adsorption experiments were conducted in a batch system. To determine the optimum adsorption pH, effect of dye concentration, the absorption kinetic coefficient and isotherm constants were determined. In each case, the absorption capacity was obtained using the following equation (Dang *et al.*, 2009):

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

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 concentration of the dye on the adsorption was assessed for 7 hours in order to determine the coefficients of adsorption kinetic and isotherm constants.

Data resulted were analyzed using the equations of Langmuir isotherms, Freundlich, Dubinin-Radushkevich and kinetic equations of pseudo-first-order kinetics and pseudo-second-order and the rate constants and the abovementioned isotherms constants were extracted to interpret the processes of adsorption, adsorption capacity, type of adsorbent and its energy. All chemicals used were obtained from Merck. All the experiments were repeated twice and all containers used were pickled and finally were washed with deionized distilled water to reduce errors.

3. Results

We used two types of acid (sulfuric and phosphoric) to modify clinoptilolite. XRF results (Table 1) showed that the raw clinoptilolite was affected and changed by the acid, and this modification changed the rate of dye adsorption. As it is clear from the figures 1 to 3, modified zeolites have higher adsorption efficiency compared with raw clinoptilolite. However, clinoptilolite modified with sulfuric acid showed better adsorption efficiency compared with clinoptilolite modified phosphoric acid. The equilibrium adsorption capacity of clinoptilolite increases as the dye initial concentration increases.

In fact, the more solution concentration in terms of number of ions, the better absorption. In addition, it was indicated that the adsorption kinetics of DR23 dye was relatively fast at the beginning of the process, but overall the process is relatively slow, and it reaches equilibrium finally, after about 130 to 200 minutes. Based on these results, 200 minutes time was considered as the equilibrium time of adsorption reaction. Therefore, the maximum adsorption of dye for initial concentrations of 50, 100, 150, and 200 mg/l was achieved to be 0.09, 0.15, 0.17, and 0.18 mg/g for raw clinoptilolite; 0.25, 0.38, 0.43, and 0.40 mg/g for phosphoric acid-modified clinoptilolite, and 0.30, 0.47, 0.57, and 0.62 mg/g for sulfuric acid- modified clinoptilolite, respectively. Figure 4 shows the effect of pH on the adsorption of the DR23 using clinoptilolites modified with phosphoric acid and sulfuric acid. Regardless of the type of modified clinoptilolite, minimum adsorption efficiency occurred at alkaline pH, so that changing pH from 4 to 9 resulted in decreasing dye adsorption based on C_t/C_o ratio from 0.62 to 0.37 and 0.53 to 0.36 when phosphoric acid modified and sulfuric acid modified clinoptilolites were used respectively.

Table 2 presents Q_e and K_L obtained using linear regression. Coefficient of determination (R^2) for raw clinoptilolite, phosphoric acid-modified and sulfuric acid-modified clinoptilolite was found to be 0.95, 0.98, and 0.99 percent respectively, indicating excellent fitness of monolayer Langmuir model for dye adsorption using acid modified clinoptilolites.

We used Freundlich multi-layers adsorption model to evaluate the data obtained and the Freundlich constant coefficient and bf were achieved by linear regression (Table 2). It was found that the Freundlich model well describes DR23 adsorption as Langmuir adsorption model. The thermodynamic parameters of DR23 adsorption were achieved according to the Dubinin-Radushkevich relationship and E value equaled to 11 to 13 KJ/mol. We used pseudo-first-order and pseudo-second-order kinetics for data descriptions of the adsorption process. Table 3 shows the rate constant values for different concentrations of dye and related kinetics.

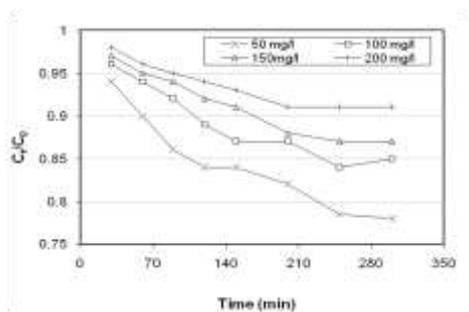


Figure 1: Effect of initial concentration on adsorption of DR 23 by raw clinoptilolite in various contact time (pH= 4, adsorbent dose= 10 g/l)

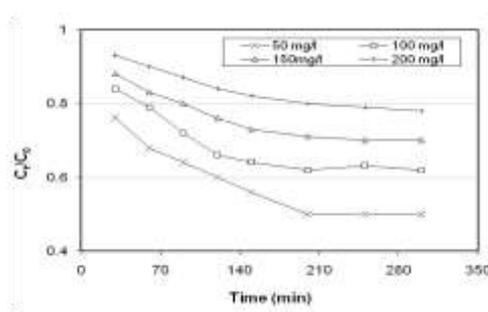


Figure 2: Effect of initial concentration on adsorption of DR 23 by modified clinoptilolite with phosphoric acid in various contact time (pH= 4, adsorbent dose= 10 g/l)

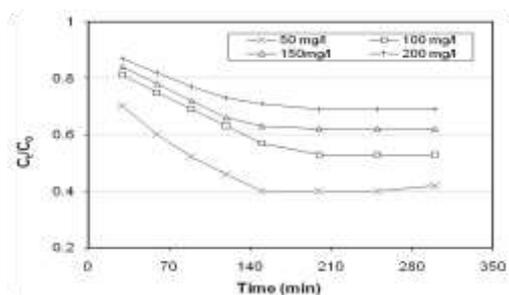


Figure 3: Effect of initial concentration on adsorption of DR 23 by modified clinoptilolite with sulfuric acid in various contact time (pH= 4, adsorbent dose= 10 g/l)

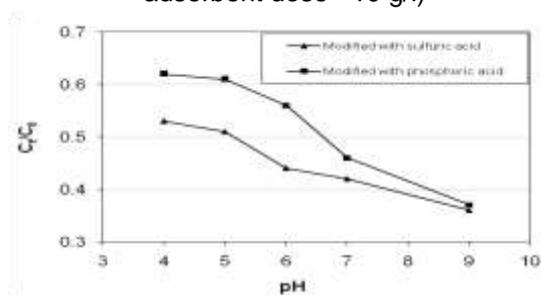


Figure 4. Effect of pH on adsorption of DR 23 by acid modified clinoptilolites ($C_0=100$ mg/l, $t=200$ min, adsorbent dose= 10 g/l)

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

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. Q_e * (mg g ⁻¹)	Pseudo first order			Pseudo second order		
			Cal. Q_e ** (mg g ⁻¹)	K_i (min ⁻¹)	R^2	Cal. Q_e ** (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

4. Discussion

Zeolite is a mineral with a crystalline structure and possesses abundant microscopic pores. The main effect of zeolite to adsorb is ion-exchange properties. Other mechanism such as surface charge of the porous structure of the zeolite is a special feature of absorbing material. However, the color removal efficiency by zeolite is not as well as clay. As other researchers have pointed out, raw clinoptilolite zeolite has low capacity for reactive dyes adsorption. In this regard, Armagan *et al* used Turkey clinoptilolite zeolite to remove three Everzol Black, Everzol Red and Everzol Yellow dyes. Their studies showed that this adsorbent has limited and low adsorption capacity (35, 25, and 35%, respectively (Armagan, 2004). Therefore, we used two types of acids (sulfuric and phosphoric) to modify zeolite. Acid modification will increase the pore volume in zeolite, reduce the surface negative charge, and will increase the hydrophobic property of zeolite (Gevorkyan *et al.*, 2002; Armagan, 2004).

One of the factors effective in adsorption capacity is the ratio of silicon to aluminum in the zeolite lattice structure. This ratio in natural clinoptilolite is 5.6, which increased to 6.1 and 7.6 after modification with phosphoric and sulfuric acids respectively. The increase in this ratio in modified forms increases the time to reach break point and the saturation point. It is also known as silica to alumina ratio of the clinoptilolite modified by sulfuric acid and phosphoric acid, is further amended by clinoptilolites and clinoptilolite adsorption capacity of this increase has been modified with sulfuric acid. Moreover, the mineral acids increase surface area by removing impurities existing inside the clinoptilolite lattice structure.

In an adsorption process, the initial concentration of adsorbate ions in solution has a key role as a driving force to overcome the mass transfer resistance between liquid phase and solid phase. It is, therefore, expected that the amount of dye adsorbed ions increases with increasing the initial concentration of the dye. As it is clear, changes in pH is effective on the adsorption of DR23, because the solution pH has effect on both the surface charge of the adsorbent and the charge of the dye adsorption, which are controlling the conditions. DR23 is an anionic dye with negatively charged surface due to having negative sulfonate groups in its molecular structure. Clinoptilolite zeolite has negative charge, which typically does not allow the dye to approach the adsorbent surface (Armagan *et al.*, 2003). Now, increasing pH makes the adsorbent surface highly negative reducing dye adsorption due to the hydroxyl ions in the net charge medium of the adsorbent surface. The adsorbent dose had direct effect on the adsorption of DR23. Increasing dosage of the adsorbent made the adsorption active sites to increase. However, the amount of dye adsorbed per unit mass of adsorbent (mg/g) shows a decreasing trend. The decrease in adsorption capacity with increasing adsorption is due to the large number of sorption unsaturated sites. In fact, increasing adsorbent amount would make the adsorbent sites remain free due to the limited dye solution (Bulut and Aydin, 2006; Wan Ngah and Hanafiah, 2008).

Adsorption isotherm is one of the most important factors in system design. The adsorption isotherm describes the interaction between adsorbent and adsorbate. It is always an important factor for determining the adsorption capacity and optimizing the use of adsorbents considered. The coefficient of determination (R^2) for dye adsorption onto raw zeolite, phosphoric acid and sulfuric acid-modified clinoptilolite was 0.95, 0.98, and 0.99 percent respectively, indicating a good fitness of the Langmuir monolayer model for dye adsorption using clinoptilolite modified by phosphoric acid and sulfuric acid. On the other hand, it is well matched with mathematics and it may be due to homogeneous distribution of adsorption sites on the surface of adsorbent because the Langmuir isotherm assumes that adsorbent surface homogenous. Although the Langmuir monolayer model was fit for describing imperial data, the process was also evaluated using Freundlich model and we found that this model fits the process very well like Langmuir. Regarding the isotherm, the line gradient resulted from the linear regressing data revealed that the adsorption average free energy (E) for adsorbing desired dye using raw clinoptilolite, phosphoric acid and sulphuric acid modified clinoptilolite was 11.2, 12.9, and 12.9 KJ/mol. In the case of adsorption process, an E value between 8 to 16 KJ/ mole is to be concluded that the adsorption process follows chemical ion exchange and if the value of E is less than 8 KJ/mole,

physical adsorption process dominates adsorption (Dang *et al.*, 2009). Therefore, the adsorption of DR23 was conducted under chemical adsorption mechanism.

The adsorption kinetics were assessed in order to better understanding the adsorption dynamic and a anticipating model, which allows estimating the ions adsorbed during the process. The values of the absorption rate constant (K_i) and the pseudo-first-order kinetics along with Q_e calculated by the equations derived from experiments for different dye concentrations are shown in Table 3. As these tables indicate, considering R^2 , it can be concluded that the linear regression is an acceptable description of the experimental data. However, in many DR23 concentrations used, the Q_e calculated is much smaller than the actual (obtained from experiments) value of Q_e . Although the pseudo-first-order kinetic is quite fit for describing practical data, but it is less accurate for predicting Q_e . Therefore, we used pseudo-second kinetic adsorption for adsorption kinetic analysis. Moreover, the Q_e calculated is not close to the practical Q_e (resulted from the experiment). Therefore, pseudo-first-order kinetics expresses the adsorption process better than the pseudo-second-order kinetic.

5. Conclusions

The efficiency of natural zeolite (clinoptilolite) and acid modified zeolite as a low-cost adsorbent on removal of Direct Red 23 from aqueous solution using a batch adsorption experiments was evaluated. Surface modification of zeolite was carried out using two acids, sulfuric acid and phosphoric acid, to improve the removal efficiency of dye solution. Results showed that modified zeolites have higher adsorption efficiency compared with raw zeolite. However, zeolites modified with sulfuric acid showed better adsorption efficiency compared with zeolites modified phosphoric acid. Based on the results of equilibrium studies, 200 minutes time was considered as the equilibrium time of adsorption reaction. Regardless of the type of modified zeolite, minimum adsorption efficiency occurred at alkaline pH. Using the adsorption data, the parameters of Langmuir and Freundlich adsorption isotherms were determined and it was found that the equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Moreover, dye adsorption using zeolite followed pseudo first-order kinetics. The adsorption results indicated that natural zeolite has a limited adsorption capacity for direct dye but it was distinctly improved by modifying its surfaces using sulfuric acid. The thermodynamic parameters of DR23 adsorption were achieved according to the Dubinin-Radushkovich relationship and E value equaled to 11.2 to 12.9 KJ/mol.

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