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Zaman Ageel HAMMOOD[1], Tasnim Fahim CHYAD[1] and Rasha AL-SAEDI[1*]

ADSORPTION PERFORMANCE OF DYES OVER ZEOLITE FOR TEXTILE WASTEWATER TREATMENT

Abstract: Removal of textile dyes from wastewater have recently attracted much attention, due to the toxicity, difficult visibility, and thereby the negative consequences on the aqueous environment. Therefore, there have been diverse promising new techniques such as adsorption for dyes removal from industrial wastewater. Compared to the highly cost treatment techniques, removal of dyes using the adsorption process is relatively simple and requires less cost. Synthetic zeolite was used in this research as a high capacity nano-adsorbent for the removal of reactive dyes from coloured wastewater. The impact of main parameters: dose of adsorbent (0.0025 to 0.02 g), pollutant concentration (25 to 200 mg/L), contact time (10 to 120 minutes), degree of agitation (25 and 300 rpm), and solution pH (2 to 8) on adsorption performance of the synthesised zeolite was investigated. The optimum values of these parameters to remove dyes efficiently at 90 % removal were 0.02 g, 200 mg/L, 80 min, 300 rpm, and 6-7 respectively. Also, two models were evaluated, the Langmuir and Freundlich isotherms. Langmuir isotherm was more efficient for representing the data than the Freundlich. The results of the Langmuir isotherm gave K_L = 0.08 L/mg, q_m = 6.02 mg/g, and R^2 = 0.98, which fitted to the adsorption data of zeolite. Reactive dye adsorption by synthetic zeolite is a vital tool in identifying the fate of dye removal from industrial wastewater treatment plants.

Keywords: reactive dyes, textile wastewater, synthetic zeolite, adsorption

Introduction

According to an estimate, textile industry uses up to 10,000 various types of dyes, with a mass yield up to $7 \cdot 10^5$ tonnes/year and a loss of 10-15 % dyes in dying textile water. Many organic and toxic constitutes are usually generated from textile industries, which have consequently posed a significant toxic and carcinogenic impacts on the aquatic systems [1]. In the textile industry, dyes are sorted into three major categories: (a) Anionic dyes: comprised of reactive, direct, and acidic dyes, (b) Cationic dyes: including all basic dyes, and (c) Nonionic incorporate dispersed dyes. Among various types of dyes utilized in such industry, the use of reactive dyes is widely spread due to their chemical stability, a preferred property of bright colour, solubility in water, simplicity in utilization and low energy demand [2]. However, dye removal is still an obstacle, as most dyes are biodegradable-resistant. Furthermore, the disposal of these coloured compounds without treatment, is aesthetically displeasing, an obstacle for light penetration [3]. Therefore, removal of such dyes prior to discharge is strongly recommended [4, 5] in order to meet the requirements of wastewater treatment and disposal [1, 6].

[1] Department of Environmental Engineering, College of Engineering, Mustansiriyah University, P.O.BOX 46049, Baghdad, Iraq, phone +9647704381656, ORCID: ZAH 0000-0002-3094-8690, TFC 0000-0002-0654-8355, RAS 0000-0002-5371-4715

[*] Corresponding author: rasha.az2013@gmail.com, rasha.azeez@uomustansiriyah.edu.iq

At a commercial scale, different techniques were implemented to treatment such dyes including, biological methods, chemical oxidation, precipitation, and coagulation; still less practical owing to the complexity and high cost. However, physical and chemical treatment technologies are prevalent for the removal of such dyes. Physical adsorption is greatly effective for the decolourization of dye wastewater; because of the simplicity in design and operation, cost effective, high removal efficiency, and ecofriendly [2, 6].

Various researchers have used natural or freely available absorbents for the removal of dyes from industrial wastewater such as waste shell, moringa seed [7], waste red mud [8], coal, clay, and peat [9]. However, zeolite is a crystalline aluminosilicate microporous material, with characteristics of high cation exchange capacity and surface area, creating a three-dimensional matrix with related pores [10], which make it more efficient than the natural absorbents with a dye removal efficiency up to 94 % from wastewater [9]. Furthermore, zeolite can be used several times without the loss of activity. The regeneration of zeolite can be achieved by several methods such as, Fenton oxidation and high temperature combustion. However, the regenerated adsorbents usually show different capacities depending on several factors such as, the elected regeneration technique, time, temperature, and pH [11].

Freundlich and Langmuir isotherms have been widely employed to demonstrate an equilibrium between liquid and solid phases in the ion exchange process of dyes [12].

In this study, the influence of adsorbent dosage, contact time, pH, agitation speed, and initial dye concentrations were examined to provide insight on the optimum conditions of reactive dyes adsorption onto zeolite. The Freundlich and Langmuir isotherm studies were also evaluated for representing the experimental data.

Materials and methods

In this research, the characteristics of zeolite used as an adsorbent medium are illustrated in Table 1. The manufactured dye was obtained from Al-Nasseg factory - Babylon city.

Zeolite specimens were grounded, passed through a 300 µm sieve, and dried in an oven at 100 °C for 24 hours. For the examination of adsorption behaviour of 100 mL of the dye aqueous solution on 0.0025 gram of the prepared zeolite, batch tests were carried out. Samples were kept stirring at 200 rpm for 2 hr. In order to compute the quantity of dye removed from aqueous solution, centrifuge of suspension was accomplished, then the supernatant was transferred and filtered through 0.45 µm membrane filters in order to separate the sorbent from the aqueous solution. Thereafter, a 10 mL of the filtered solution was obtained for the determination of dye concentration via Genesys-10 spectrophotometer. To determine the optimum conditions of the involved parameters, the experiment was performed at various conditions of initial dye concentrations (from 25 to 200 mg/L), contact time (10-120 minutes), shaking velocity (250 and 300 rpm), zeolite dosage (from 0.0025 to 0.02 gram), and pH (from 2 to 8). All sampling was done in triplicate.

Under equilibrium conditions, the weight of dye adsorbed Q_e [mg/g], was computed using below equation [13]:

$$Q_e = \frac{C_0 - C_e}{W} \cdot V \quad (1)$$

where: C_0 - initial concentration of dye [mg/L], C_e - concentrations of dye at equilibrium [mg/L], V - volume of the solution [L], W - mass of adsorbent [g].

Table 1

Physical and chemical properties of zeolite

Property [unit]	Values
Porosity [-]	0.34
Cation exchange capacity [meq/100 g]	17.9
Surface area [m^2/g]	437
Pore volume [cm^3/g]	0.26
Bulk density [g/cm^3]	0.6
Particle density [g/cm^3]	1.1
Particle size [mm]	1-3
Al_2O_3 [%]	29.0
TiO_2 [%]	1.5
Na_2O [%]	13.0
CaO [%]	2.5
SiO_2 [%]	34.3
Loss on ignition [%]	15

Results and discussion

The ion exchange process between a solution and the solid surfaces occurs when a joint reaction occurred between the charged species of the adsorbate and adsorbent, with an exchange in the anion / cation, as the molecules approach. Thus, an interconnection among dissolved organics, solvent molecules, and surfaces of adsorbents entirely take place. The experiment was conducted at various solid / liquid fractions at initial dye concentration of 25 mg/L and a period of 2 hours.

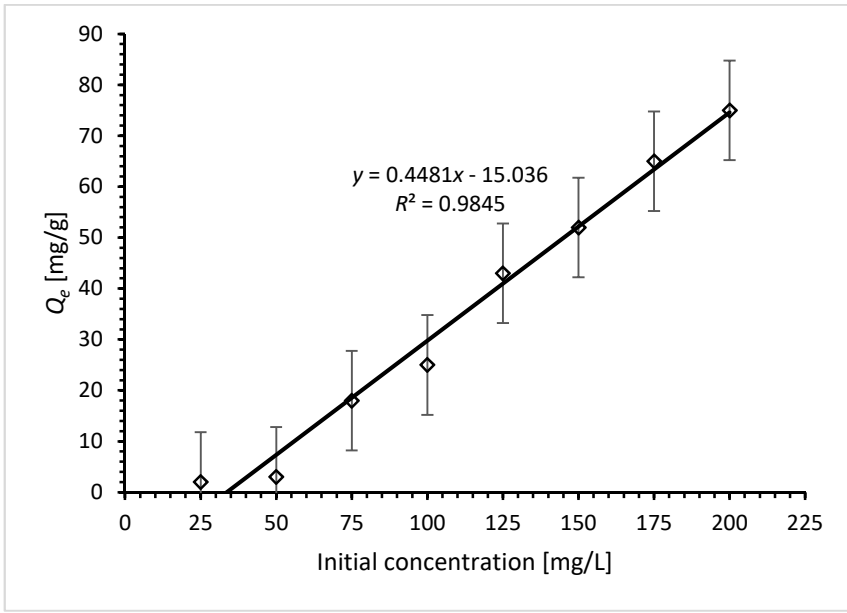


Fig. 1. Relationship between initial dye concentration and dye adsorption

Figure 1 shows adsorption of dye onto zeolite under initial dye concentrations ranging from 25 to 200 mg/L. Ammonium exchange was enhanced with increasing the initial concentrations of dye. This resulted in excessive molecules of dye, which are bordering the sorbent places and therefore complementing the magnitude of mass transfer between the adsorbed solute and adsorbent substance [6, 14]. Also, the large surface area and permeable character might enable more adsorption sites for occupation; therefore, promoting the ability of adsorption from 20 to 75 mg/g with heighten the dye concentration to 200 mg/L. These results are in accordance with that previously investigated research by Akgul and Karababakan [14], Bazrafshan et al. [15], Al-Jerf [1], Tony [6].

The phenomenon of the improved adsorption capacity can be elucidated as follow: exchange of dye ions occurs at locations of higher energy with low ratios of dye-ion / adsorption. Raising the dye ion / adsorption fraction led to a saturation of higher energy areas and adsorption takes place at fewer energy areas, with a decline in the ion exchange process efficiency [1, 14].

To determine the typical time for approaching stability, the experiment was carried out at time intervals of 10, 20, 30, 40, 50, 60, 80, and 120 min at a constant concentration of dye (50 mg/L). Figure 2 shows that as the contact time progressed, the adsorption weight of dye over zeolite intensified, this could be due to the insufficiency in the internal diffusion resistance and an adequate access to the exchange sites. After about 60 min, the adsorption intensity becomes gradually unchanged, giving an evidence that empty surface places for exchange could not be noticed [16]. Approaching the period of stability, in conjunction with a notable removal implied that the large affinity of the amended adsorbent to the reactive dyes [14]. The equilibrium time 69 min at Q_e = 8 mg/g to adsorb dye on zeolite was found similar to the results stated by Bazrafshan et al. [15], Mirzadeh et al. [17], Jafari and Mahvi [18], Kim et al. [19], Konicki et al. [12] and Aljerf [1].

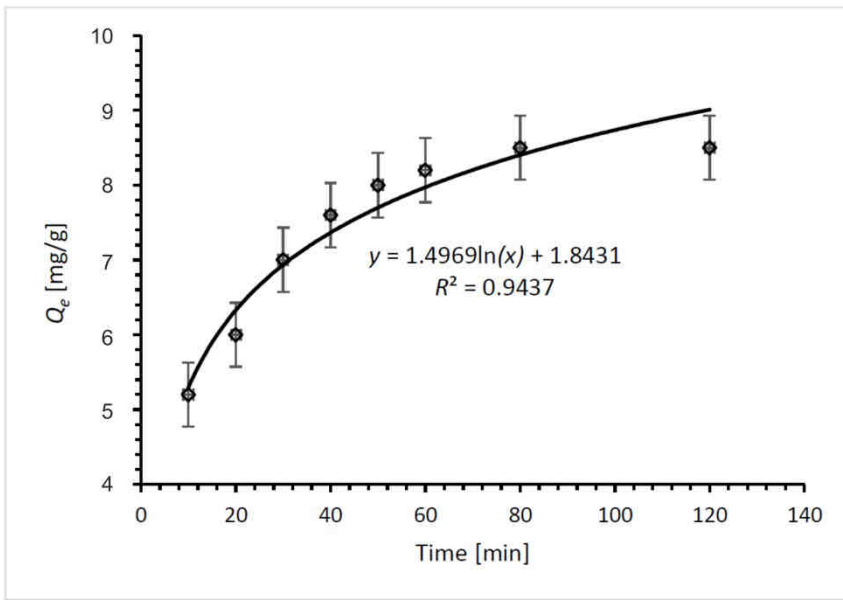


Fig. 2. Dye adsorption over the contact time

As pH is a powerful variable in the dye adsorption mechanism; the effect of pH was therefore studied by varying the initial pH levels at 2, 6, 7, and 8, under an initial constant concentration of 50 mg/L. Figure 3 shows an improvement in the adsorption capacity of dye with raising the pH level, a favoured adsorption was however accomplished at pH levels between 6-7. When pH varied from 2 to 6, the ion exchange upgraded from 6 to 18 mg/g. Promoting adsorption at neutral pH levels might be due to the electrostatic reaction between the negatively charged medium and cationic dyes [11, 20, 21]. At low pH levels, lower Q_e magnitudes were obtained; because of the competitiveness between H^+ with the molecules of charged dye for the unoccupied exchange areas [14]. The obtained data is in accordance with results documented in the studies [2, 14, 22-24]. However, at higher pH levels, the adsorption efficiency dropped from 18 to 10 mg/g, reflected that pH value of 8 was not favoured to accomplish the optimum adsorption under the experimental conditions.

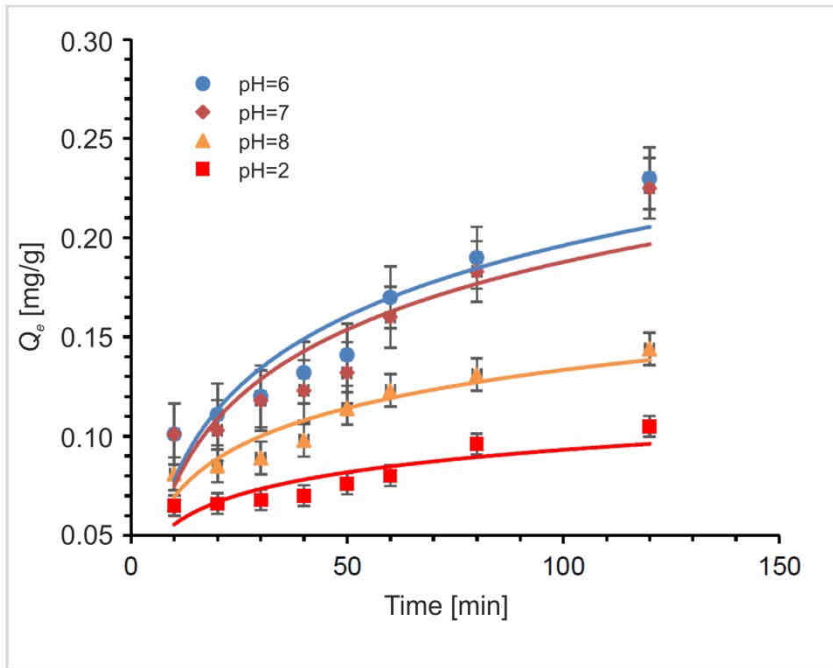


Fig. 3. pH influence on dye adsorption

In order to investigate the influence of solid mass on the adsorption of reactive dyes, this experiment was undertaken for a range of synthetic zeolite mass (from 0.0025 to 0.02 g) at an initial constant dye concentration of 25 mg/L.

Figure 4 shows that the adsorption density enhanced with much supplement of the solid dosage, this trend of dye removal can be attributed to the overall increment in the adsorbent's specific surface area (active sites of exchange) [1, 23, 26]. In this experiment, this dosage was higher than the dose applied by Armagan et al. [4] who also studied adsorption of reactive dye on synthetic zeolite.

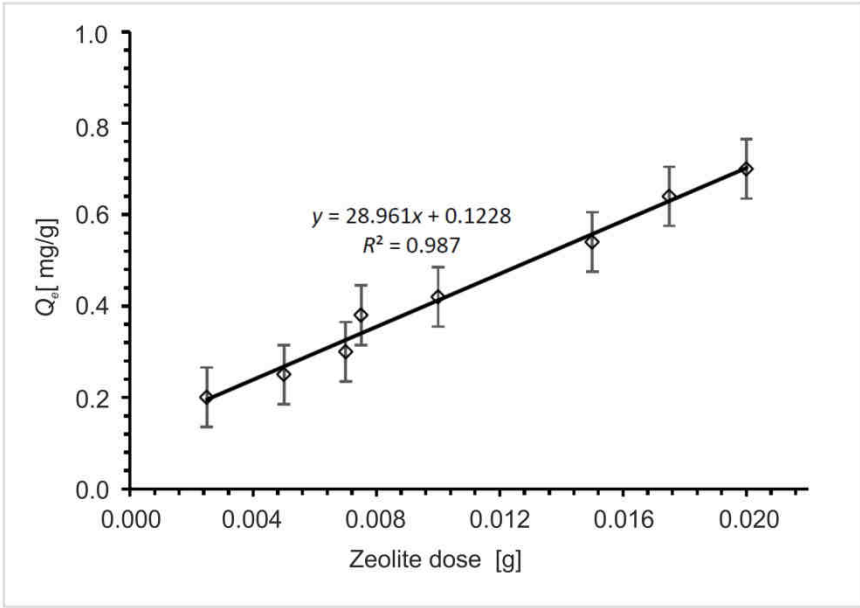


Fig. 4. Influence of zeolite dose on dye adsorption

Table 2 shows the result obtained from adsorption of reactive dyes onto synthetic zeolite under two agitation speeds over the experimental period. The rate of dye removal was slightly influenced by lowering the degree of agitation from 300 to 250 rpm. However, Garg et al. [27] conducted adsorption experiments at various stirrer speeds aiming at dye removal using synthesised zeolite. They found that adsorption capacity enhanced with increasing stirrer speed, and considered 300 rpm as the optimal agitation speed.

Table 2

Effect of agitation speeds on dye adsorption

Time [min]	**Q_e [mg/g]***	**Q_e [mg/g]****
10	0.79	0.64
20	0.71	0.56
30	0.65	0.52
40	0.54	0.46
50	0.48	0.41
60	0.41	0.36
80	0.3	0.3
120	0.26	0.25

* agitation speed = 300 rpm, ** agitation speed = 250 rpm

The most frequently used equations for dilute solutions, which imply a correlation between the equilibrium data, are the Langmuir and Freundlich isotherms (equations (2) and (3)) [12].

Based on the Langmuir equation (implied to the equilibrium sorption), it was hypothesised that monolayer sorption onto surfaces along with a finite number of uniform places. The Langmuir isotherm can be set down as [28]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{2}$$

where: Q_m - the highest adsorption capacity of synthetic zeolite [mg/g], K_L - the coefficient of Langmuir equilibrium [L/mg].

The Freundlich equation can be written as [28]:

$$\log(Q_e) = \log K_f + \frac{1}{n}\log C_e \tag{3}$$

where: K_f and n - Freundlich coefficients.

K_f and $1/n$ are correlated to the sorption capacity and intensity of the system.

Applying the adsorption data to both isotherms, indicated that only Langmuir equation successfully represented the process under initial concentrations ranged from 25 to 200 mg/L. In contrast, dye adsorption did not conform with the Freundlich isotherm. Figure 5 shows the constants and regression coefficients of the Langmuir isotherm giving values of K_L and Q_m of 0.08 L/mg and 6.024 mg/g respectively.

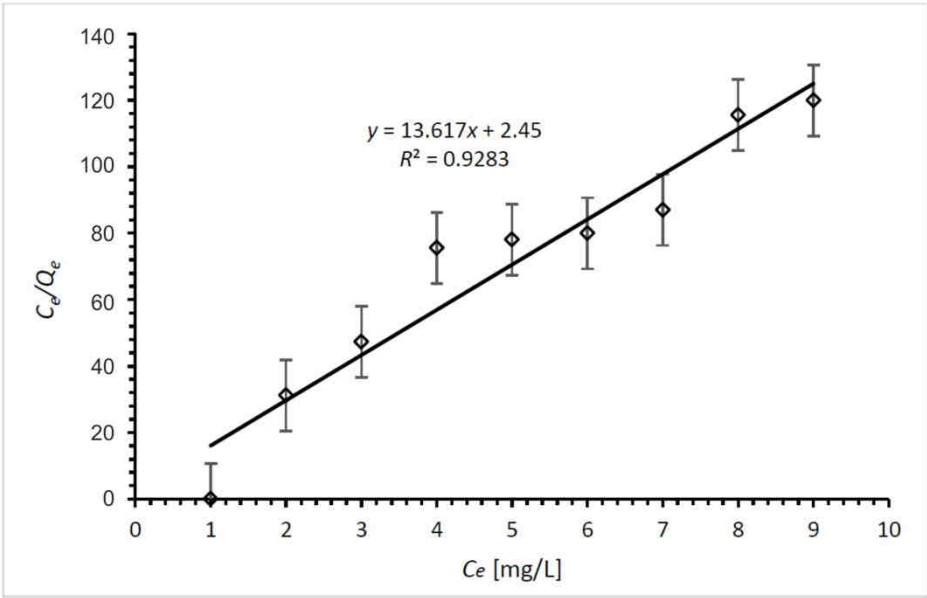


Fig. 5. Langmuir isotherm for dye adsorption over zeolite

Conclusion

The study showed that zeolite is a well competent for the uptake of textile dyes from the dye aqueous solution. The contact time of around 1 hour was adequate for approaching an equilibrium state, which revealed a high affinity of zeolite for the reactive dyes.

The results indicate that pH is a determined variable influencing the adsorption ability of the used dyes. A neutral pH was favourable for the adsorption of reactive dyes. Surface charge is a limiting factor for the exchange process of the ionic and cationic dye molecules, which is primarily controlled by pH. As pH usually enhances the negative charge over the surfaces of zeolite, which could be advantageous in terms of adsorption capacity. In contrast, lowering the pH level promotes the positive charge over the surfaces of adsorbent and enhances the electrostatic attractiveness between ions and surfaces. Adsorption capacity is conversely affected by the alkaline state and this therefore need to be investigated further.

An increment in the initial concentrations of dye led to an increase in the number of dye ions and optimization the competitiveness for approaching the binding areas at contact surfaces; whereby all places exposed to the ions were motivated. Also, with the solid dose more than 0.8 g, the ion exchange process was completely accomplished since the adsorbent was fully flooded and the solid/liquid form almost reached the steady state.

As the influence of the studied agitation speed range did not significantly show a difference, a broad range of agitation speed thus requires further investigation.

The study of equilibrium sorption isotherm revealed that Langmuir model was a well representor for the data of adsorption.

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