

Removal of Acid Red 14 by Pumice Stone as a Low Cost Adsorbent: Kinetic and Equilibrium Study

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ABSTRACT: *In this work, removal of C. I. Acid Red 14 was investigated by Pumice stone as a low cost adsorbent. Various parameters such as initial dye solution, contact time and pH were studied. Removal of dye were increased by increasing of contact time and initial dye solution and decreased by increasing of pH. Three isotherm models were studied. Linear and non-linear regression analyses were used for determination of best isotherm model. In addition, Chi-square test parameter (χ^2) was used for the comparison of experimental and calculated data that was obtained from equilibrium studies. The results of linear and non-linear regression analysis shows the removal of Acid Red 14 follows the Frundlich isotherm model ($r^2 > 0.987$, $X^2 = 11.1$). Fitting of obtained data onto kinetic models show the pseudo second order kinetic model best describe kinetic sorption of Acid Red 14 onto pumice. Mass transfer coefficient was determined at various initial dye solutions and was compared with the same work. The order of external mass transfer coefficient was 10^{-3} - 10^{-4} . De-sorption studies demonstrate low regeneration of pumice for Acid Red 14 (9.4%).*

KEY WORDS: *Adsorption, Equilibrium studies, pumice, Azo dye, Batch study.*

INTRODUCTION

Unused dyes compounds and several organic and inorganic pollutants in textile wastewater are the environmental pollution sources [1]. Many industries such as pharmacology,

food production, cosmetic activity, pulp and paper industries generate such effluent [2]. The dye used in those industries is often synthetic dye. Those dyes have

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divided into acidic, reactive, direct, basic and other group. Azo dye has an azo group band (-N=N-) and because of their low cost, variety, solubility and stability are the most common synthetic dye that have been used for dyeing [3]. It is estimated that over 50% of total produced dye in world is azo dye. It has been recognized that between 1–20% of the whole world production of azo dyes is lost during the dyeing processes and providing main wastewater pollution in wastewaters. There are aromatic rings in the azo dye molecular structures which cause these effluents to be toxic and mostly non-biodegradable; therefore, becoming an important source of environmental pollution [4]. The also with discharge Colored compounds in water, Biochemical Oxygen Deman (BOD) of water will increase, Colors also caused complete inhibition of light transmission into the water and therefore reduced dissolved oxygen rate in the water during photosynthesis [5, 6]. Without appropriate treatment, releases of such wastewater to environment are a serious problem for aquatic environment and human health. For that reason, treatment of colored waste is necessary. Several methods such as aerobic-anaerobic treatment [4], advanced oxidation [5], membrane process [6] and others have been used for dye removal from dyestuff effluents. Adsorption is a key process that has been used for the removal of pollutant from wastewater for its low cost, easy application and effectiveness [7]. Commercial activated carbon is the most common adsorbent that has been used in this process. This product is very effective for removal of pollutant but it is expensive [8]. Recently many researchers have used natural matters such as chitosan [9], oxihumolite [10], flay ash [11] and other matter as a sorbent. Pumice which is a volcanic stone has a light weight and porous structure (up to 85%) and is found in many regions of the world. Because of its microporous structure, pumice has a high specific surface area and it can float in water. Due to many advantages of pumice stone and accessibility of it in Iran, the aim of present work was to investigate removal of azo dye named Acid Red 14 (AR 14) by pumice stone.

EXPERIMENTAL SECTION

Preparation of sorbent

Pumice stone was obtained from Tikmeh Dash region of Eastern Azerbaijan (Iran). The present sorbent was

Table 1: Chemical component of present pumice (by w/w).

Component	%	Component	%
SiO ₂	51.45	SrO	0.227
Al ₂ O ₃	17.08	MnO	0.092
TiO ₂	1.54	K ₂ O	3.26
P ₂ O ₅	0.661	SO ₃	0.529
CaO	6.44	Na ₂ O	5.67
Fe ₂ O ₃	6.32	MgO	6.17

light exhibit and 85% porosity. The chemical structure of present pumice is shown on Table 1. The natural pumice was washed several times by double-distilled water and then put in 1 N HCL acid for 24 hour. After that, the pumice sample was taken and rinsed several times by double-distilled until its effluent turbidity reached under 0.1 > NTU. Finally, the prepared sample was crushed and sieved to 20 meshes and used as sorbent. The chemical structure of present sorbent was determined by X-Ray Fluorescence and is listed in Table 1. In addition the morphology of pumice stone before and after modification was characterized by SEM (Fig.1); it was characterized by an irregular structure after modification (Fig.1). The Specific Surface Area (by BET method) of modified pumice was 28 m²/g and reached to 54 m²/g after modification with acid.

Chemicals and experiments

All chemical used in this work was GR grade and obtained from Merck (Germany). The chemical structure Acid Red 14 (molecular weight: 502.42) is shown on Fig. 2. The pH of solution was adjusted by 1 N H₂SO₄ or NaOH (Sartorius PP-50). All experiments were conducted at batch system and in 250 mL conical flasks. Various parameters such as pH (3, 5, 7, 9 and 11), initial dye concentration (50-200 mg/L) and contact times were studied. For experiment, an amount of adsorbent was added onto dye solution at various pH, and then shaken at 200 rpm (Hanna-Hi 190M, Singapore). After that, at predetermined time interval the sample was taken, filtered, centrifuged and the final concentration of dye was determined by UV/VIS spectrophotometer (Shimadzo-1700, Japan) as the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

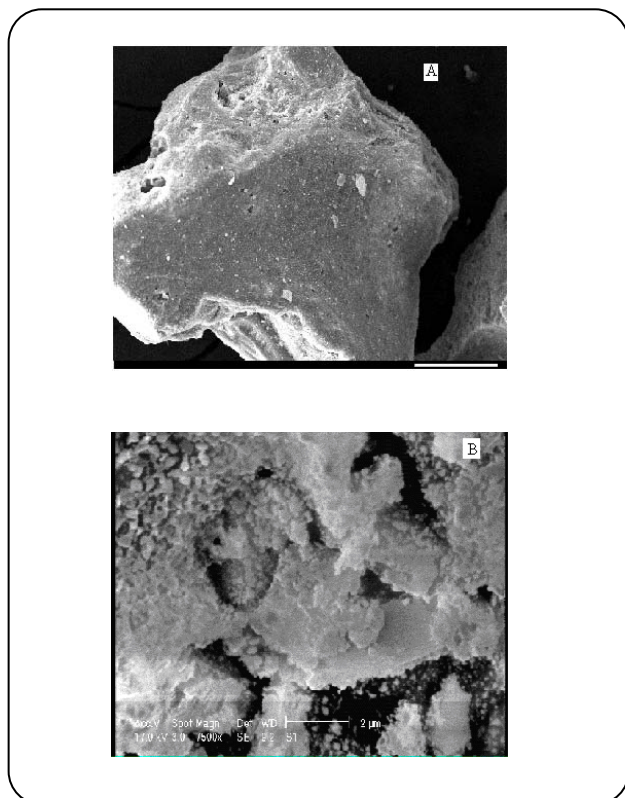


Fig. 1: SEM image of the adsorbent, pumice stone, before (a) and after (b) modification.

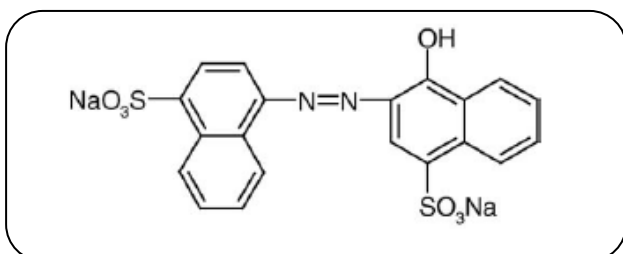


Fig. 2: Chemical structure of Acid Red 14.

Where q_e (mg/g) is the dye adsorbed on pumice, C_0 and C_e are initial and equilibrium concentration of dye (mg/L), respectively. The V (L) is the volume of solution and the M (gram) is the mass of pumice.

Equilibrium Study

The design of adsorption process is line on equilibrium experiment known as adsorption isotherm. The Langmuir and Freundlich isotherm model are commonly used for the description of equilibrium data. Langmuir isotherm model is based assumption of homogenous surface energy distribution. The linear and non-linear shape of Langmuir model is described as follow:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \text{(Non-linear form) (2)}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad \text{(Linear form) (3)}$$

Where q_e is the equilibrium amount of adsorbate (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), q_m is maximum adsorption capacity and b is the Langmuir constant. The important feature of the Langmuir model can be described by separating parameter known as R_L and expressed as following:

$$R_L = \frac{1}{(1 + b C_0)} \quad (4)$$

The values of R_L are listed as follow.

Another commonly isotherm model is Freundlich model that is used for heterogeneous system. This model is expressed as follow:

$$q_e = K_f C_e^{1/n} \quad \text{(Non-linear form) (5)}$$

$$\log(q_e) = \log K_f + 1/n \log C_e \quad \text{(Linear form) (6)}$$

Where q_e is the amount of adsorbate (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_f and $1/n$ are the Freundlich constants. The high value of K_f shows the high affinity of adsorbate. For favorable adsorption, the value of Freundlich constant (n) should be in the range of 1-10.

The Temkin isotherm is another model that has been used for heterogeneous adsorption of adsorbate on surface. The following is the non-linear form of Temkin model:

$$q_e = \frac{RT}{b_1} \ln(k_t C_e) \quad (7)$$

By rearranging Eq (7), one can present the linear form of Temkin model as follow:

$$q_e = B_1 \ln(k_t) + B_1 \ln(C_e) \quad (8)$$

Where $B_1 = RT/b_1$, b_1 is adsorption heat, k_t is the equilibrium binding constant (L/g) corresponding to maximum binding energy. By plotting q_e vs. $\ln(C_e)$ one can calculate B_1 and k_t from slope and intercept of this curve, respectively. Linear and non-linear shape of same equation has a different value for same parameters. To remove this knot, the non-linear Chi-square (χ^2) test

Table 2: The values of R_L based on adsorption type.

R_L Values	Type of process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

has been proposed. The low value of Chi-square (χ^2) test shows the agreement of experimental data by obtained once. The Chi-square (χ^2) test equation is shown as following:

$$\chi^2 = \sum_{i=1}^N \frac{(q_{e,\text{exp}} - q_{e,\text{calc}})^2}{q_{e,\text{calc}}} \quad (9)$$

Where the subscripts “*exp*” and “*calc*” show the experimental and calculated values and N is the number of observations in the experimental data. Therefore in present work both correlation coefficient (r^2) and χ^2 were used to determination of best isotherm model.

Kinetic modeling

Designing of adsorption process is lined on the kinetic study. The mechanism of chemical reaction is explained by chemical kinetic [12]. The most common kinetic models for adsorption are pseudo-first order and pseudo-second order. Recently modified pseudo-first order model was proposed by Saied [13]. In addition, intra-particle diffusion model was used by many researchers to determination of rate controlling step.

Pseudo-first order model

Pseudo-first order kinetic described by the following equation [13]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (10)$$

Where q_e and q_t are the amounts (mg/g) of adsorbate at equilibrium and at time t (min) respectively; and k_1 is the rate constant (1/min). Integration of the Eq. (10) at the boundary of $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, gives:

$$\text{Log}\left(1 - \frac{q_t}{q_e}\right) = -\frac{k_1}{2.303} t \quad (11)$$

Pseudo-second order model

Pseudo-second order kinetic is expressed as the following equation [13]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (12)$$

Where k_2 is the rate constant (g/mg min). Integration of the Eq. (12) at the boundary of $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ and then rearrangement to a linear form gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

The value of k_2 and q_e can be determined from the intercept and slope of the plot t/q_t vs. t , respectively.

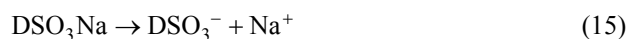
RESULTS AND DISCUSSION

Adsorption mechanism

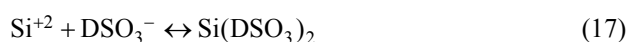
Adsorption mechanism of used azo dye can be easily described by chemical composition of adsorbent and dye. As shown in Table 1, the main component of sorbent is SiO_2 (51.45%). According to the following equation, this component in aqueous solution and at surface of adsorbent can decompose to Si^{+2} and O_2^{-2} :



Then the Si^{+2} species are formed on the surface of adsorbent. In addition, in aqueous solution acid dyes is first dissolved and then decomposed to the sulphonate groups of acid dye and anionic dye groups as following:



In the view of Eq. (14) and Eq. (15), the adsorption process continued due to electro-static interaction of DSO_3^- and Si^{+2} as two counter groups:



Moreover, in the presence of H^+ ions, this ion is added to the surface of adsorbent and increases the cationic capacity of adsorbent:



By above equation, the sorption capacity of pumice in acidic condition would be increase [14, 15].

Effect of dye solution

Dye solution of 125-200 mg/L was used. Fig. 3 shows the effect of initial dye solution on dye removal. By Fig. 2 dye removal was increased by increment of initial dye solution. These phenomena can be described

by increment in driving force with increasing of dye solution. Increment in driving force with increases of pollutant concentration has been reported by many researchers in removal of other pollutants. Removal of calcium ions by Ca-Selective zeolite was increased by increases in initial calcium concentration [16]. The same results were reported in removal of cesium by natural vermiculite [17] and removal of fluoride by sol-gel-derived activated alumina [18]. In addition, there was a low increment in dye uptake rate by increasing of initial dye concentration. One reason to low increment in dye sorption rate is due to occupation of empty site on adsorbent at initial step. As soon as empty sites were occupied, dye sorption rate would be decreased [16].

Effect of contact time

Effect of contact time on dye sorption was carried out at time interval 1-390 min and is shown on Fig. 4. By Fig. 4, removal of dye was increased by increasing of contact time and reached to equilibrium before 390 min. Dye removal was very high at initial contact time. At contact time equal 1 min, 75 % of AR 14 was removed. It can be concluded that pumice stone has high capacity for removal of AR14. These phenomena can be described by molecular weight of dye. The AR14 has a low molecular weight and so can penetrate to internal part of pumice adsorbent. Removal of AR14 by fly ash was conducted by other researchers [19]. The results of present work show the high removal of AR14 by pumice at lower contact time respect to fly ash.

Effect of solution pH

Effect of pH on dye sorption was carried out in the range of 3-11. Fig. 5 shows this effect. By Fig. 5 dye removal was decreased by increment of pH. Removal of dye was decreased from 90% to below 5% with increase in solution pH from 3 to 11. Solution pH plays an important role in the controlling of the surface charge of the adsorbent and removal of adsorbate in the solution. At low pH, the H^+ ions is predominant in solution and the surface of pumice will charged with those ions. This phenomena lead to significantly strong electrostatic attraction between the positively charged pumice stone and anionic dye molecules. Therefore at low pH, dye sorption will be high. Many researchers have been reported the same results in agreement with our work.

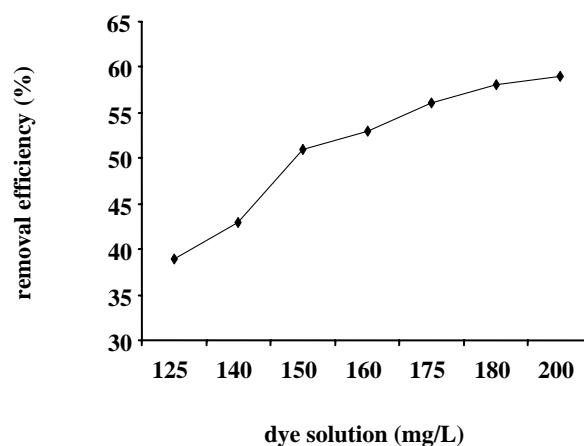


Fig. 3: Effect of initial dye solution on sorption rate (contact time=390 min, pH=3.5, Pumice=2 g/L).

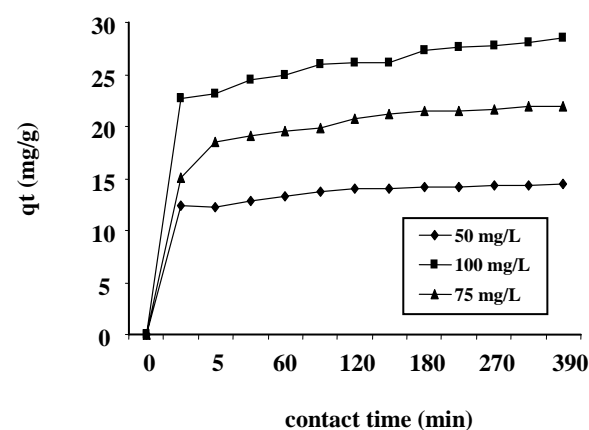


Fig. 4: Effect of contact time on dye removal at various initial dye concentration (pH=3.5, pumice=2 g/L g).

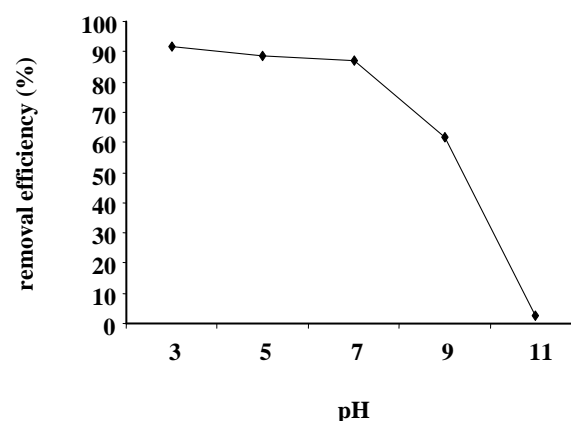


Fig. 5: Effect of pH on dye removal ($C_0=75$ mg/l, $t=390$ min, pumice=2 g/L).

Table 3: Parameters of Linear and Non-linear Fitting of isotherm model.

Linear Fitting								
	$q_m(\text{mg/g})$	$b(\text{L/mg})$	K_f	n	$RT/b_1(\text{kJ/mol})$	$k_1(\text{L/mg})$	R^2	χ^2
Freundlich	-----	-----	23.93	3.76	-----	-----	0.987	13.3
Langmuir	58.824	0.415	-----	-----	-----	-----	0.977	168.7
Timken	-----	-----	-----	---	9.189	13.171	0.942	47.3
Non-linear Fitting								
Freundlich	-----	-----	23.187	3.53	-----	-----	0.987	11.1
Langmuir	52.492	0.661	-----	-----	-----	-----	0.835	137.6
Timken	-----	-----	-----	-----	9.206	13.063	0.943	47.3

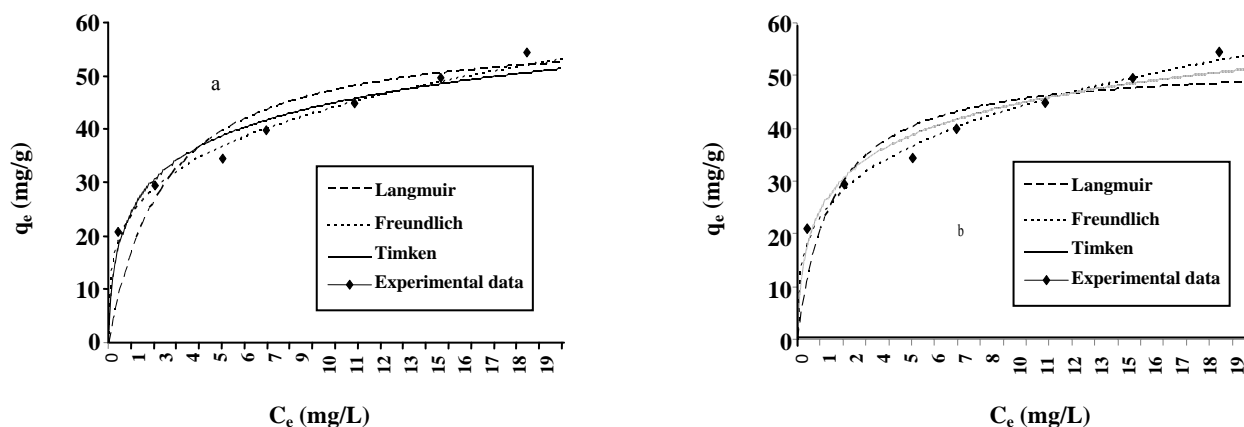


Fig. 6: Isotherm model for present work (a=linear fitting, b=non-linear fitting).

Removal of acidic dyes onto cationic polymer-loaded bentonite was reported to be high in acidic pH (pH=2) [20]. Removal of Congo red by cattail root [21] and Remazol Yellow Gelb 3RS and Basic Yellow 37 by chitosan derivatives [22] were reported to be high in pH= 2.2 and pH=2.5, respectively.

Adsorption isotherm

Linear and non-linear fitting of adsorption isotherm model for present work is shown on Fig.6. The values of isotherm parameters are presented in Table 3. Based on correlation coefficients (r^2), the Freundlich isotherm model best describes the AR14 sorption onto pumice by both linear and non linear regression analysis. But for remove the error of linear and non-linear form of same equation, the Chi-square (χ^2) value was used. Based both correlation coefficients (r^2) and Chi-square (χ^2) value,

the sorption of AR14 follows the non-linear form of Freundlich isotherm model ($r^2 > 0.987$, $\chi^2 = 11.1$). The maximum capacity of present medium was 52.49 mg/g. The value of R_L and n were 0.1 and 3.65; showing the Favorable sorption of present work. In addition the maximum sorption capacity of present work was 55 mg/g, namely higher than those reported in published work [23].

Kinetic study

Fig.6 shows the kinetic model for present work and related parameters are listed in Table 4. As shown in Table 4, pseudo second order kinetic model best describe sorption of Acid Red 14 onto pumice stone. In addition, it was demonstrated that the obtained value of q_e from kinetic model was the same as obtained from the equilibrium experiments.

Table 4: Parameters of kinetic models.

Pseudo first order	$k_1(1/\text{min})$	$k_2(1/\text{min})$	$q_e(\text{mg/g})$	r^2
$C_0=50\text{ mg/L}$	0.013	-----	14.5	0.88
$C_0=75\text{ mg/L}$	0.011	-----	22	0.96
$C_0=100\text{ mg/L}$	0.007	-----	29	0.95
Pseudo second order				
$C_0=50\text{ mg/L}$	-----	0.35	14.47	0.999
$C_0=75\text{ mg/L}$	-----	0.242	22	0.999
$C_0=100\text{ mg/L}$	-----	0.187	28.4	0.999

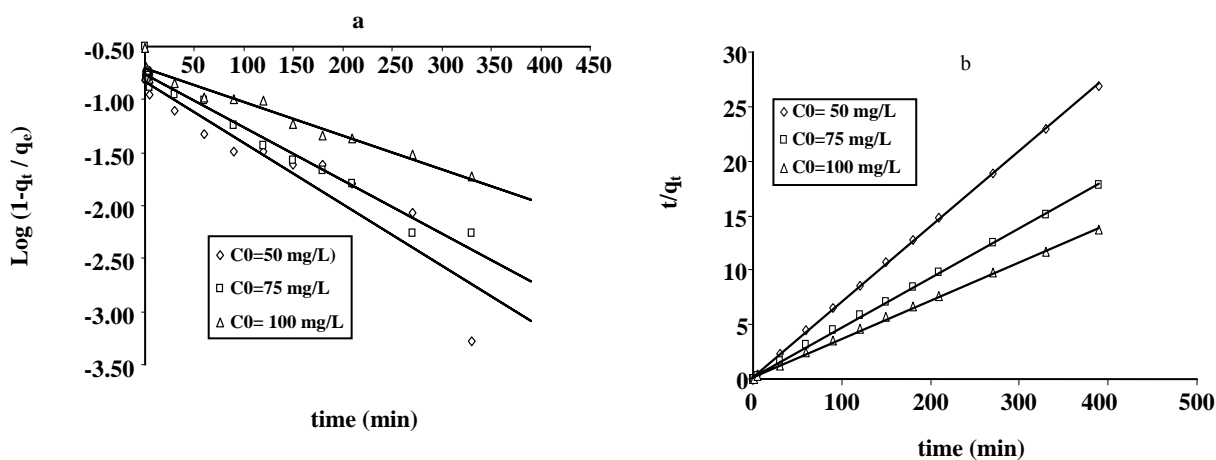


Fig. 6: Kinetic models for present work (a: pseudo first order, b: pseudo second order).

MASS TRANSFER COEFFICIENT

In adsorption process there are two basic mass transfer resistances named as external diffusion and internal diffusion. The external mass transfer is expressed as:

$$N_t = k_f A(C_t - C_s) \quad (19)$$

Where N_t is the diffusion rate pass the film layer around the adsorbent particle, A is the external surface of adsorbent, C_s is the adsorbate concentration at equilibrium time, C_t is the adsorbate concentration at time t and k_f is the external mass transfer coefficient. The reverse value of k_f indicates the resistance in the film layer. Based on mass balance equation, diffusion rate can be expressed as:

$$N_t = -VdC_t / dt = mdq_t / dt \quad (20)$$

At initial condition, Eq. (20) can be rearranged to the following:

$$(N_t)_t \rightarrow 0 = k_f AC_0 \quad (21)$$

Using initial shape of pseudo-second order kinetic model, Eq. (20) and Eq. (21), one can arrive to the following:

$$k_f = mkq_e^2 / (C_0 A) \quad (22)$$

Eq. (22) is the overall shape of such equation to calculate external mass transfer coefficient, k_f [24, 25]. The external mass transfer coefficient at various initial dye solutions is listed in Table 5.

The result of external mass transfer coefficient was in order of 10^{-3} - 10^{-7} . Other researchers obtained external mass transfer coefficient in the order of 10^{-4} that agree with the results of present work [24, 25].

De-sorption

De-sorption experiment was conducted 250 mL beaker. About 0.5 gram of adsorbent was added into 250 mL

Table 5: Mass transfer coefficient at various initial dye solutions.

C ₀ (mg/L)	70	100	120	140	160	180	200
k _f (cm/s)	0.002	0.0002	3.6×10 ⁻⁵	2.27×10 ⁻⁵	1.09×10 ⁻⁵	6.71×10 ⁻⁶	4.7×10 ⁻⁶

of dye solution of 160 mg/L and stirred at 200 rpm for 390 min. After that, the sample was taken and it is determined about 93% of AR 14 was removed. To investigate de-sorption process, the adsorbent from previous step was taken, rinsed several times and heated at 150 °C for 6 hours. This adsorbent again was added to 250 ml of 160 mg/L dye. After 390 min contact time, the sample was taken and it was cleared the final concentration of dye. In this term, the final concentration of AR 14 was 146 mg/L. The following equation was used to calculate regeneration of used pumice:

$$A = \left[\frac{(B - C)}{B} \right] \quad (23)$$

Where A is the percentage of non-regenerated adsorbent, B and C are the percentage of dye adsorbate before and after regeneration, respectively. By Eq (23), the regeneration degree of pumice for AR 14 was 9.4%. The low regeneration degree for AR 14 can be described by high affinity of AR 14 ($k_f=23.187$) that was obtained from isotherm studies.

CONCLUSIONS

Removal of Acid Red 14 was investigated by pumice stone as natural matter that is found in many regions of Iran. The followings are the main results of present work:

- Dye removal was increased by increasing of contact time and initial dye concentration and decreased by increscent of pH.
- Linear and non-linear egression analysis shows the removal of Acid Red 14 follow Freucndlich isotherm model ($r^2>0.987$, $X^2=11.1$).
- Adsorption mechanism was proposed effectively based on molecular weight, sulphonate groups, chemical structure of adsorbent and dye.
- External mass transfer coefficient was determined and compared with similar work. It was in order of 10^{-3} - 10^{-4} that agrees with previously conducted work.
- Kinetic data was best fitted onto pseudo second order model

- A simple and effective regeneration method was proposed and examined for regeneration of used pumice.

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