Removal of Reactive Red 120 and Direct Red 81 dyes from aqueous solutions by Pumice

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Abstract

Dyes are the main pollutants existing in wastewater of textile industries. Dyes are produced naturally or artificially and can cause fabrics to take different colors. The main objective of this work was to investigate adsorption of Reactive Red 120 (RR 120) and Direct Red 81 (DR 81) dyes by pumice. This fundamental-practical study was conducted in lab-scale batch system. Chemical structure and composition of Pumice was determined by X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and electronic microscope. The effects of contact time and initial solution pH on adsorption process were also evaluated. The Freundlich and Langmuir isotherms were used to describe adsorption equilibrium. The results of adsorption isotherm experiments show that the removal of RR120 and DR81 dyes follow Langmuir (R2>0.964) and Freundlich (R2>0.932) isotherm models. It was found that the affinity coefficients, Kf, for DR81 and RR120 dyes were 10.56 and 2.32 respectively, indicating higher adhesion of pumice to DR81 than RR120. In general, the results of the study showed that pumice can be used as a cheap and effective adsorbent for removal of dye from textile industrial effluents.

Keywords: Adsorption, Pumice, isotherm, Direct Red 81, Reactive Red 120.

Introduction

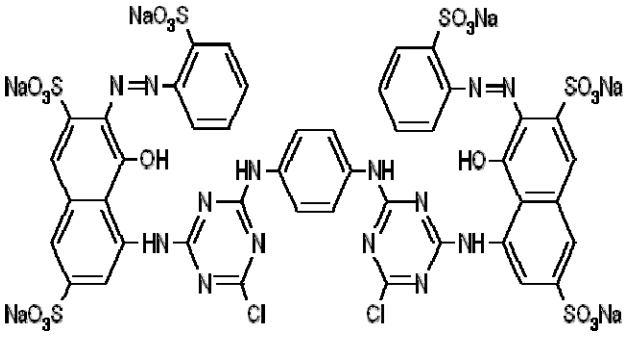
Dyes are the main pollutants of textile industries. They are dominantly organic compounds that are produced naturally or artificially. These substances can cause fabrics to take different colors through various dying stages[1]. About 1 to 20% of total global production of dyes is lost during dyeing processes and released into textile wastewaters. The principle classes of dyes based on their chemical structure are acidic, alkaline, reactive, disperse, azo, diazo, anthraquinone and metallic dyes[1-2]. Despite the fact that textile industry effluents contain several pollutants, wastewaters with high color levels have devoted considerable attention. They are mainly organic material and contain two or more benzene rings causing resistance against decomposition. The existence of such rings in the dye compounds makes them toxic. A wide range of structurally diverse dyes are used in textile industry. Some of them are more degradable and less toxic whereas others are less degradable and more toxic[2-3].

Generally, synthetic dyes are divided into acidic, reactive, direct, basic and other groups[3].Although different dyes are used in industries, azo and reactive classes are by far the most commonly used dyes[4-5]. The azo dyes are widely used in textile, leather and food industries and characterized by one or more azo bonds (-N-N-)[6-7]. Till now, a wide variety of methods including biological treatment[8-9], membrane[10], advanced oxidation[6,11-12], photo catalytic processes[11-13] and adsorption[14] processes have been used for treatment of such effluents. However, adsorption process is one of the most common processes used in water and wastewater treatment.

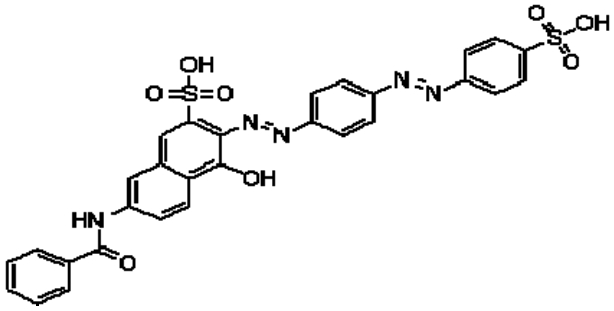
The adsorption process is commonly done using activated carbon. Commercial activated carbon is typically expensive and its application needs trained and expert operators. To date, many researchers have studied natural adsorbents such as chitosan[15], oxihumolite[16], fly ash[17], iron-coated activated carbon[18] etc. in order to remove organic and inorganic pollutants from aqueous environments. Pumice is a volcanic rock that is a solidified form of volcanic lava and can be found in many places around the world. Also, in Iran, this rock can abundantly be found in many parts mostly in Azerbaijan. Pumice has high porosity, light weight and normally either floats on water or sinks slowly. It has high levels of silica, about 60-70 percent of weight. Silica with the chemical formula of SiO_2 is quartz. The Mohs Hardness for pumice is 5-6[19]. In this study, the performance of Pumice in adsorption of Reactive Red 120 (RR120) and Direct Red 81 (DR81) dyes is better. The RR120 and DR81 dyes were selected as representative for azo class dyestuffs. Regarding wide industrial usage of RR120 and DR81 dyes, particularly in textile industry, we have also investigated the removal of these compounds from aqueous solutions by pumice which is an effective and cheap adsorbent. The physicochemical and morphological characteristics of pumice were analyzed by scanning electron micrographs (SEM) and XRF (X-ray fluorescence).

Material and Methods

Chemicals: This fundamental-practical study was conducted in lab-scale batch system. All reagents used in preparation and adsorption studies were obtained from Merck Company. Reactive Red 120 (RR120) ($C_{44}H_{30}C_{l2}N_{14}O_{20}S_6$) and Direct Red81 (DR81) ($C_{29}H_{19}N_5Na_2O_8S_2$) dyes (99% purity) were supplied by Alvan Sabet Company (Hamadan, Iran) and were used without further purification. The chemical structures of the dyes are shown in fig. 1.



(a)



(b)

Fig.1: Chemical structure of azo dyes: a) RR120 and b) DR81

The adsorption of DR81 and RR120 by Pumice was modeled with Freundlich and Langmuir adsorption isotherms. Adsorption rates of dyes were measured using +UV/vis spectrophotometer (Shimadzu 1700, Japan) at the maximum wavelength (λmax) of 536 and 509 nm for RR120 and DR81 dyes respectively. pH was adjusted using either H_2SO_4 or NaOH solutions (1 N) (Sartorius PP-50). Adsorption isotherms and capacities were determined through batch experiments used to describe the kinetics of adsorption process. The adsorption capacity was calculated using eq. (1):

$$q_e = \frac{(C_0 - C_e)\, V}{M} \qquad (1)$$

where C_0 and C_e are the initial and final concentrations of dyes in aqueous solution (mg/l) respectively, V is the volume of dye solution (L) and M is the mass (g) of pumice used.

Preparation of adsorbent: Pumice used in this experimental research was taken from East Azarbaijan in Iran. It was washed several times with distilled water to remove initial impurities. In order to enhance the porosity, the material was placed in contact with 1N HCl for 24 hours. Conditioned Pumice was again washed with distilled water until effluent turbidity reached to less than 0.1 NTU. The prepared material was grounded and sieved. The particles with effective size of 2 mm (mesh size of 20) were considered as the adsorbent material.

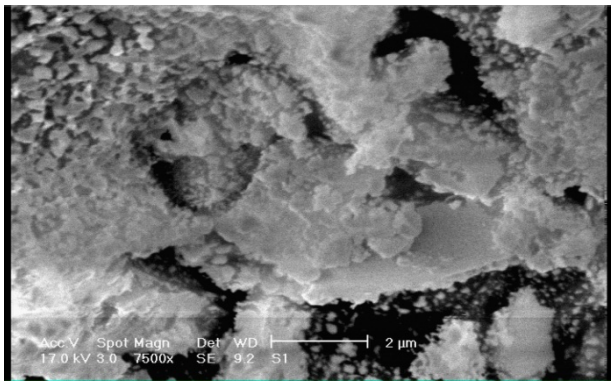


Fig.2: Scanning electron microscopic image of pumic sample

Chemical composition of pumice samples was determined by X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). The results for this analysis are given in table 1 and figure 2. The XRF and SEM experiments showed that the pumice is composed mainly of quartz, SiO_2, (74 wt %). The results are consistent with those of other studies[19,20]. Microscopic image of adsorption sites was also taken using a SEM-XL30 (Philips, The Netherlands) and given in figure 3.

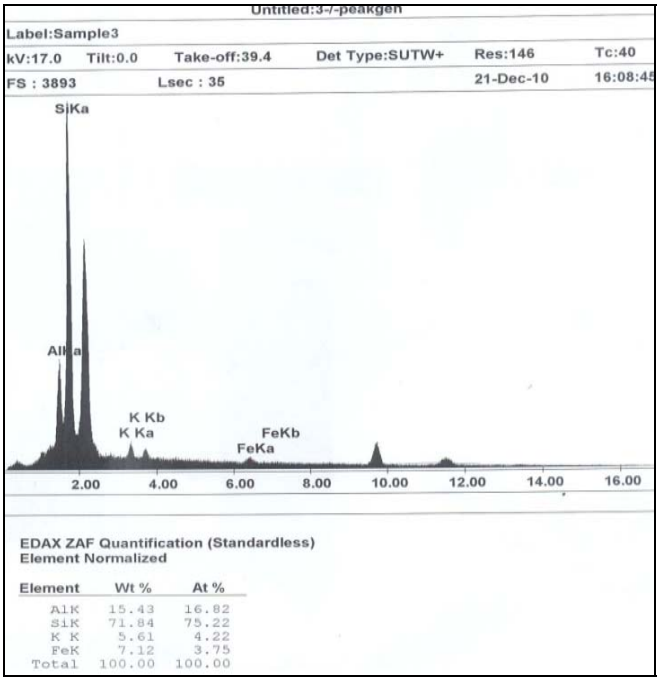


Fig.3: Microscopic image and SEM analysis of adsorption sited on pumice

Results and Discussion

Effect of contact time on the adsorption of dyes: Effect of contact time was evaluated at time periods ranging from

1 to 180 min and initial dye concentration of 50 mg/L (initial adsorbent dose of 0.5 g at pH 5). The effect of contact time on removal of RR120 and DR81 dyes is shown in figure 4. As seen in figure 4, the dyes removal rates increased with increasing contact time and reached equilibrium after 60 min. Maximum removal efficiency (53.36%) and adsorption capacity (8 mg/g) of DR81 and maximum removal efficiency (48.73%) and adsorption capacity (7.31 mg/g) of RR120 were occurred after 120 and 150 min respectively. Therefore, it can be concluded that the removal efficiency for DR81 by pumice is higher than that for RR120.

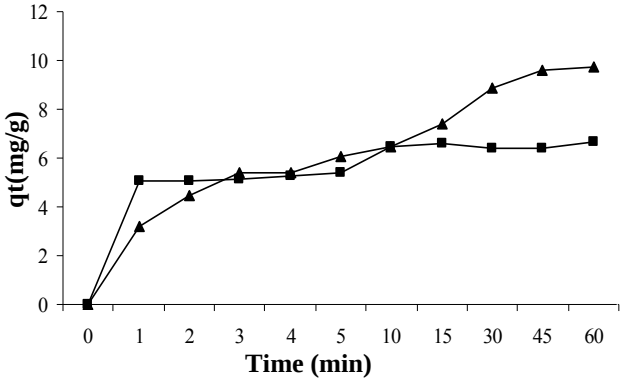


Fig.4: Contact time versus adsorption capacity for RR120 and DR81 (adsorbent dose: 0.5 g per 150 ml sample at pH 5)

Effect of pH on the adsorption of dyes: In adsorption process, pH has a major effect on surface properties and surface loading of the adsorbent. In order to evaluate the effect of pH, dye solutions with initial concentration of 50 mg/L were prepared at pH 3, 5, 7 and 9. Then, 0.5 g of pumice was then added to 150 ml dye solution. After 60 min, residual concentration of dyes was determined by Spectrophotometer. The effect of pH on the adsorption process is illustrated in figure 5. Maximum adsorption of RR120 and DR81 dyes is higher in acidic pH. As the pH of solution increased, the removal efficiency and consequently maximum adsorption of subjected dyes were decreased. Optimal adsorption of RR120 and DR81 dyes by pumice occurred at pH 3. As shown in figure 5, maximum adsorptions of RR120 and DR81 dyes in pH 3 are 11.38 and 12.58 mg per g pumice respectively.

Therefore, it can be concluded that in the same condition, the removal efficiency for DR81 by pumice in different pH values is higher than that for RR120. The current study found that the removal efficiencies of DR81 and RR120 dyes from aqueous solution through adsorption by pumice decrease with increasing initial pH of solution. In fact, higher adsorption at low pH values is due to higher H^+ ions and then higher positive charges on adsorbent surface. The positively charged surface sites tend to sorb anionic dyes through electrostatic forces[21-22]. This phenomenon occurred between the dyes studied and pumice. Consequently it was demonstrated that optimal removal of the dyes occurs in acidic condition (i.e. at pH 3.0). Moreover, the results of kinetic experiments showed that the adsorption of RR120 and DR81 followed pseudo second-order kinetic model.

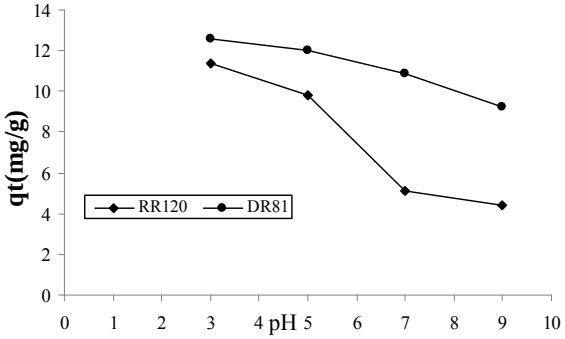


Fig.5a: The effect of pH on adsorption capacity of RR120 and DR81 (adsorbent dose: 0.5 g per 150 ml sample, initial dye concentration: 50 mg/L, contact time: 60 min)

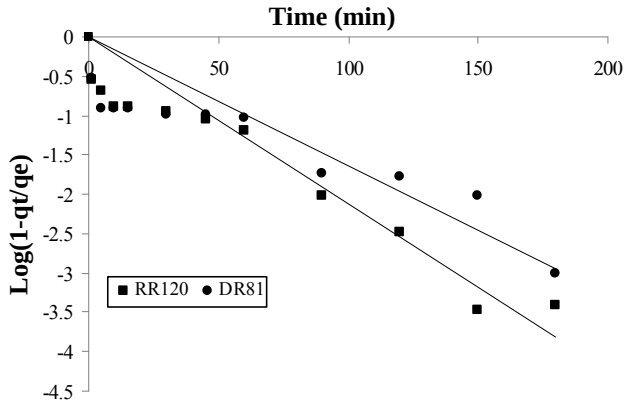


Fig.5b: Fit of the experimental data to Pseudo first order kinetic model plot for RR120 and DR81 dyes

Adsorption isotherms: Langmuir and Freundlich isotherm equations have been used by many researchers to describe adsorption isotherm of numerous dyestuffs on various adsorbents. The adsorption isotherms are the relationships that describe adsorbate distribution between the solid and aqueous phases at equilibrium. To determine the best fitting isotherm model, 0.5 g of adsorbent was added to dye solutions having initial dye concentrations ranging from 50 to 200 mg/L. Afterward, the solutions were thoroughly mixed and centrifuged at 200 rpm for 120 min. Residual dye concentrations were then measured using UV-vis spectrophotometer at λmax of 536 and 509 nm respectively for RR120 and DR81 dyes.

In the current study, the equilibrium experimental data of adsorbed dyes have been evaluated for compliance with Langmuir and Freundlich adsorption isotherms. Linear form of Langmuir isotherm assumes that adsorption occurs on homogeneous surface by monolayer sorption without

interaction between sorbed molecules and the maximum adsorption corresponds to a saturated monolayer of solutes on the adsorbent surface[21]. Linear form of Langmuir isotherm has the following form:

$$\frac{c_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} c_e \qquad (2)$$

where q_e is the adsorption capacity (mg-dye/g-adsorbent), C_e is equilibrium concentration of the dye in solution after adsorption (mg/L), q_m is maximum adsorption capacity (mg-dye/g-adsorbent) and K is Langmuir adsorption constant (L/mg) estimated from the intercept and slope of the linear plots of C_e/q_e versus C_e. A dimensionless constant called separation factor, R_L, was calculated to characterize the Langmuir isotherms as follows:

$$R_L = \frac{1}{(1 + bC_0)} \qquad (3)$$

where C_0 is the initial dye concentration (mg/L). The value of R_L indicates the nature of adsorption isotherm (Table 2). Freundlich isotherm can be used for non-ideal sorption that occurs on heterogeneous surface. The isotherm assumes that the adsorbed amount of solute infinitely increases with increasing its concentration in solution. The linearized Freundlich isotherm is expressed as follows[23]:

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \qquad (4)$$

where q_e is the adsorption capacity (mg-dye/g-adsorbent), C_e is equilibrium concentration of the dye in solution after adsorption (mg/L), K_f and 1/n are Freundlich constants that are the measure of sorption capacity and intensity respectively. 1/n values indicate the type of adsorption and it may be irreversible (1/n=0), favorable (0<1/n<1) or unfavorable (1/n>1). Freundlich isotherm is nonlinear when 1/n<1[19-20]. 1/n and K_f are determined from the slope and intercept of plots of log q_e versus log C_e.

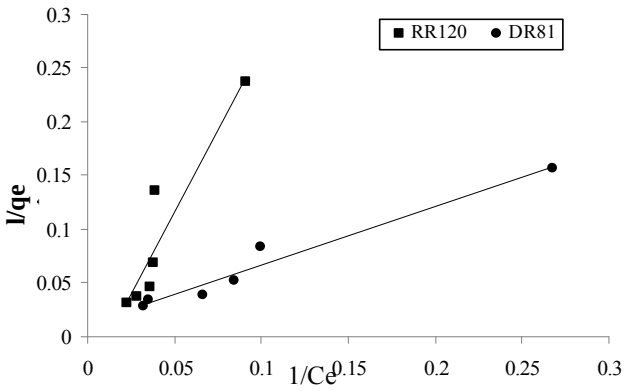


Fig.6a: Langmuir isotherm plots for adsorption of RR120 and DR81

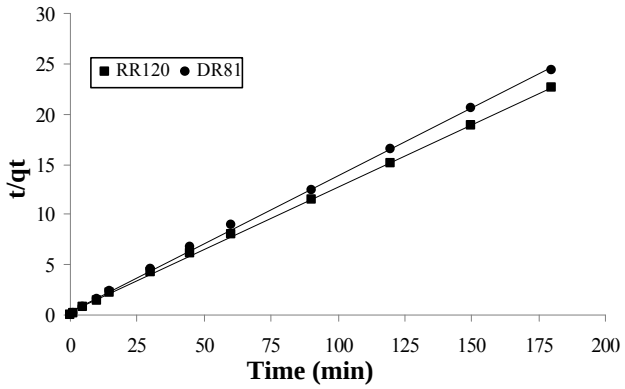


Fig.6b: Fit of experimental data to Pseudo second order kinetic model for RR120 and DR81

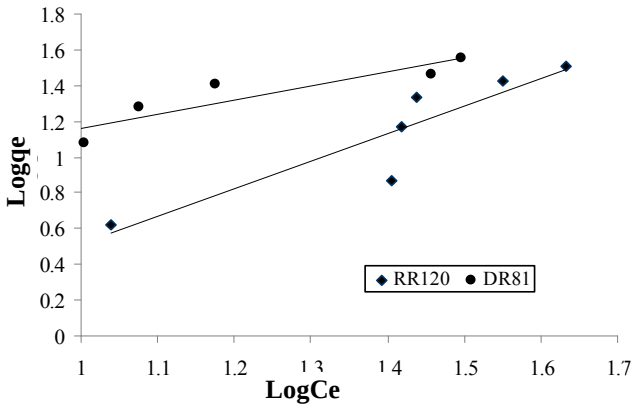


Fig.7: Freundlich isotherm plots for adsorption of RR120 and DR81

The Langmuir and Freundlich isotherms plots for the adsorption of RR120 and DR81 dyes are illustrated in figures 6 and 7 respectively. The calculated parameters of isotherms together with correlation coefficients (R_2) are summarized in table 3.

The results of adsorption isotherm experiments show that the removal process of RR120 and DR81 dyes follows Freundlich (R_2> 0.932) and Langmuir (R_2>0.964) isotherms respectively. This means that DR81 and RR120 dyes tend to be adsorbed on homogeneous and heterogeneous sites respectively[24-25]. Based on derived equation for Freundlich isotherm, respective values of K_f and n for RR120 were 2.32 and 1.54 while for DR81 were 10.56 and 0.64 respectively. Results indicate higher affinity of pumice for DR81 than RR120 and consequently more favorable adsorption. Separation factor, R_L, values for dyes adsorption by pumice can be calculated using equation 3 which yielded the values 0.01 and 0.09 for RR120 and DR81 respectively.

The maximum adsorption capacities of RR120 and DR81 by pumice were 0.32 and 1.83 mg-dye/g-pumice, illustrating higher adsorption of DR81. This condition may be due to lower molecular weight of DR81 that causes

faster adsorption of dye molecules into pumice particles[23-24]. In the current study, the maximum adsorption capacities of RR120 and DR81 increased with decreasing pH of solution. Also, it was found that the removal efficiency of dye increases with increasing contact time. The maximum adsorption capacities of DR81 and RR120 were occurred after 120 and 150 min respectively. This may be due to different molecular weights of the dyes.

Because of lower molecular weight of DR81 and its higher affinity to pumice than RR120 counterpart, DR81 can penetrate easily into pumice pores while RR120 is adsorbed only on surface layers of the adsorbent. The adsorption of DR81 and RR120 dyes at initial minutes occurs in higher rates and its rate reduces with time. This phenomenon can be explained by reduction in dissolved dye concentration and number of surface active sites of adsorbent that most of them are empty in initial steps of adsorption process and are occupied by dye molecules over time. As a rule, adsorption capacity increases with time but it becomes constant at a certain period of time. After this time, adsorption and desorption processes of the dyes will reach equilibrium[24,26].

Kinetic Models: Kinetic studies of adsorption describe solute uptake rates at different contact times. The rate-limiting step and factors affecting adsorption can be determined by performing a series of kinetic experiments at different conditions[13,25]. Pseudo first- and second-order adsorption models were used to analyze adsorption kinetics of RR120 and DR81 on pumice.

Pseudo first-order kinetic model: The nonlinear form of pseudo first-order kinetic model is expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5)$$

Integrating equation 5 for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t gives

$$Log(1 - \frac{q_t}{q_e}) = -\frac{k_1}{2.303} t \quad (6)$$

where k1 is the pseudo first order rate constant (min-1), qe and q_t are amount of absorbed dye (mg/g) at equilibrium and t=0 respectively. The fit of the experimental data to pseudo first order kinetic model for RR120 and DR81 dyes is shown in figure 5.

Pseudo second-order kinetic model: The pseudo second-order kinetic model is expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (7)$$

Integrating equation 7 for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \quad (8)$$

where k_2 is the pseudo second order rate constant (g/mg.min), k_2 and q_e can be determined from the slope and the intercept of plots of t/q_t versus t. The fit of the experimental data to pseudo second order kinetic model for RR120 and DR81 dyes is shown in figure 6.

In the present investigation, the pseudo first- and second-order adsorption models were used to analyze experimental data for adsorption of RR120 and DR81 dyes on pumice (Figures 5 and 6). Based on the overall results shown in table 4, the adsorption kinetics of RR120 and DR81 dyes on pumice followed pseudo second-order kinetic model (R2>0.99).

Conclusion

It was found that pumice can be used for sorption of both RR120 and DR81 dyes from aqueous solutions. However pumice is more effective in removal of DR81 than RR120 and maximum adsorption capacity is higher for DR81. Also, it can be concluded that pumice stone can be successfully used as a cheap adsorbent in dye removal from textile industry effluents.

Acknowledgement

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Table 1
Chemical composition of Pumice (wt %) obtained from XRF analysis

SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	CaO	MgO	Total
74.00	14.72	4.66	3.65	1.98	1.16	0.37	**100.00**

Table 2
The nature of adsorption isotherm in different R_L values

Nature of adsorption process	R_L value
Unfavourable	R_L>1
Linear	R_L=1
Favourable	0<R_L<1
Irreversible	R_L=0

Table 3
Isotherms parameters and correlation coefficients for isotherm equations

Dyes type	Langmuir isotherm				Freundlich isotherm		
	q_m(mg/g)	b(L/mg)	R^2	R_L	K_f	n	R^2
RR120	0.32	3.08	0.88	0.01	2.32	1.56	0.932
DR81	1.83	0.54	0.964	0.09	10.56	0.64	0.826

Table 4
Kinetic parameters for the adsorption of RR120 and DR81 on pumice

Kinetic equations parameters		Pseudo first order kinetic model		Pseudo second order kinetic model		
		$K_1(min^{-1})$	R^2	K_2(g/mg.min)	q_e (mg/g)	R^2
dyes	RR120	0.009	0.872	0.068	3.81	0.990
	DR81	0.006	0.630	0.085	3.42	0.990

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