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Red Reactive 2 Dye Removal from Aqueous Solutions by Pumice as a Low-Cost and Available Adsorbent

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Background & Aims of the Study: Azo dyes are used in industrial processes such as textile industry to produce large quantities of colored effluents that contain organic and non-organic materials. So, effective and efficient treatment of them is important for the environmental protection. The aim of this study was to evaluate the efficiency of powder and granular pumice for the removal of red reactive 2 in an aqueous solution.

Materials & Methods: This is an experimental study on a laboratory scale. Powder and granular pumice were prepared in a laboratory condition as an adsorbent. The study conducted on synthetic samples that contain red reactive 2 dye. The efficiency of pumice in powder and granular form, with different concentration, pH and contact time was tested.

Results: Absorption of red reactive 2 is a function of the amount of adsorbent, impressed by pH and contact time. By increasing the amount of adsorbent from 0.5 to 2 gr, the absorption rate increased around 50% to 96%. The maximum uptake for each of testing procedures was accrued in acidic solution (pH=3) and 40 minute contact time. Langmuir and Freundlich isotherms models were derived from the experimental procedures.

Conclusions: The results showed that the efficiency of powders form was better than granules. Due to the abundance of quarries in Iran, it could be used as a useful adsorbent in wastewater.

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Background

Nowadays, by developing the technology and industry based on knowledge and innovation of new products, the consumption of synthetic dyes in many industries such as producing cosmetics, leather, paper and textile have been increased.

Dyes consumption in industrial processes leading to production of significant volumes of organic and non-organic colored effluents. Efficient treatment of them is important for the environmental protection (1). Dyes stuff of industrial waste are considered, due to the high toxicity of colored industrial wastewaters on aquatic organism, impaired performance of conventional wastewater treatment system and environmental aesthetic (1,2). Discharge of industrial wastewater, containing dye industry in acceptor water leads to eutrophication and interact with acceptor water ecology (3-5). Regarding to the health, some dyes have carcinogenic and mutagenic properties, and they can cause allergies and skin problems

(5,6). Reactive dyes and pigments used in textile industries with wastewater that contain pesticides, constitute the largest group of environmental pollutants. Release of these substances in nature is a serious threat for aquatic system. Due to the cycle structure of Azo dyes, most of them are stable and resistant to biodegradation and are often toxic, carcinogenic and mutagenic (1,2,7). Dye removal from industrial wastewater is possible by various methods such as coagulants, flocculation, biological treatment, ion exchange and adsorption process (8). The adsorption process used various materials such as granular and powder form of activated carbon, bentonit soil, coal, coke and china clay. Among various absorbent, activated carbon is one of the most effective materials that used for dye adsorption. Since the process and regenerate of activated carbon is expensive and due to its waste at different stages of restoration (9), most researchers are looking for a new and cheap adsorbent and a lot of researches are being done for the development and efficiency of low-cost absorbent for the removal of dyes from wastewater industry (4). Among these absorbent, we can use the seeds of fruits like peaches (2), olives and other materials such as charcoal (7), biological solids (10), perlite (11), blue spikes of wheat, (3,13) etc. Pumice stone is a form of silica glass with bright or dark color (13). It can be found in mountainous area of Iran like north west, west, central and south. Also, in addition to the above areas, this mineral can be found in Taftan Mountains in southern of Iran, Abeali region in the north and around the Qazvin city, and also in the west of the Hamadan, Iran. Italy, with about 40 percent of total production of pumice stone is in the first place and Turkey is in the second (14). Due to its affordable price and abundance, this stone is readily available. Pumice is also a light matter (with the density of 0.5-1 kg/l) with a high porosity (vacant pore size are to 85%). This type of stone has a porous structure. This property makes the adsorption process possible (13).

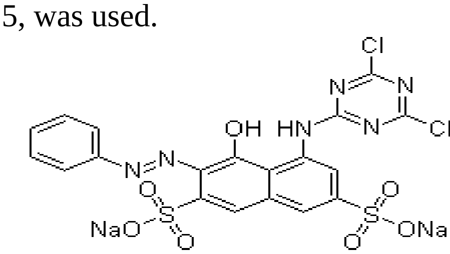
Aims of the study:

In this study, we try to use powder and granular form of pumice for the removal of red reactive 2 from industrial waste water.

Materials & Methods

This experimental study has done in order to investigate the removal of red reactive 2 dye by pumice and volcanic rocks and evaluate the effect of pH, time and initial concentration of dye solution. Adequate amounts of mineral pumice were prepared. For the preparation of adsorbent, the amount of natural granules was washed with distilled water until the impurities washed away. Then dried the washed granules at 103 ºC for 6 hours, until the moisture content was removed. Then it was crushed by mill (modelA11 BASIC) and Sieved by 200µm split screen laboratory (model DG-fcibntific-PRODUCTS-CO); in fact granules and powders were separated. To determine the composition of the pumice, ray diffraction technique (XRF) X-Ray Fluorescence, BELEC-GmbH GmbH model made by Germany were used.

Red reactive 2 dye: A red reactive 2 (C.Ic Reactive Red 2) manufactured by Merck of Germany with the chemical formula of $C_{19}H_{10}CL_2N_6O_7S_{22}Na$ and molecular mass of 33.615, was used.



Preparation of solutions: To prepare a standard solution, 1 gr of dye by double distilled water in the volume of 1000 cc was prepared. Then to provide a 0.25 ppm colored solution, 1cc of 0.25 ppm standard solution with distilled water was prepared in volume of cc1000

To prepare 0.5 and 1 ppm solution respectively 2cc and 4cc of 0.25 ppm standard solution in 100volume was prepared.

Testing method: To determine the effect of pH on the removal of dye, 0.25 ml of dye solution with concentration of 0.25, 0.5 and 1 ppm have been set in 1.5gr adsorbent with pH 3, 5 and 10. Then stirred it for 10, 20 and 30 minute on a shaker. All tests were performed on the basis of standard methods of water and waste water (15). To study the effect of contact time on the removal of dye concentration, an adsorbent with 0.5, 1 and 1.5 gr concentration was added to the dye solution with 0.25, 0.5 and 1 ppm concentration. The mixture was placed in contact with each other in burette for 10, 20, 30 and 40 minute. Then to determine the concentration of dye at a wave length of 650nm, absorption measurement and analysis were performed by spectrophotometer. All tests repeated 3 times and a total of 486 samples were tested. For reliability in each tests, devices were calibrated by standard solution. To measure the efficiency uptake of absorption, we used 1 and 2 formulas.

$$\%R = \frac{Ci - Cf}{Ci} \times 100 \qquad (1$$

$$q = \frac{Ci - Cf}{m} \times V \qquad (2$$

R: adsorption efficiency
q : adsorb uptake per unit mass of adsorbent(mg/g)
C_i: initial concentration of adsorb (mg/l)
C_f: residual concentration of adsorb (mg/l)
m: mount of adsorbent (g/l)

The equilibrium isotherms: In fact Langmuir adsorption isotherm is an estimation of the single-layer coating materials on to the external surface of the adsorbent. Nonlinear relationship of Langmuir equation is as follows (16,17):

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e}$$

C_e: Ultimate equilibrium concentration (mg/l)
b: Langmuir constant (dm^3/mg)
Q_0: maximum adsorption capacity (mg/g)

One of the features of the Langmuir equation is dimensionless parameters of separation coefficient that have a formula as below:

$$RL = \frac{1}{(1 + bC_0)}$$

RL: separation coefficient
C_0 : initial concentration (mg/l)
b : Langmuir constant
By using these parameters, we can specify the type of adsorption process.

Table1) Grading separation coefficient of adsorbent that is consistent with Langmuir adsorption model

Type of adsorption process	RL parameter
Irreversible	RL=0
appropriate	0<RL<1
linear	RL=1
Inappropriate	RL>1

Freundlich model is based on monolayer adsorption on heterogeneous adsorption sites and have the unequal energy. It has a single layer and multi-layer adsorption applications. Freundlich isotherm nonlinear equation is as below (18):

$$q_e = K_f C_e^n$$

q_e: concentration of adsorbed dye (mg/g)
C_e: ultimate equilibrium concentration (mg/g)
n,k,f: constant that respectively related to the adsorption capacity ((mg/g) (dm^3/g) n) and adsorption intensity.
Excel software was used for data analysis.

Results

Structural characteristics of pumice

XRF results showed that the main structure of pumice is formed by quartz (SiO_2)

Table 2) Pumice spectral components by XRF analysis

component	percentage
SiO_2	46.05
Al_2O_3	23.72
K_2O	5.66
Na_2O	2.65
Fe_2O_3	0.98
CaO	3.16
MgO	0.32
total	100

The effect of contact time on the removal efficiency of red reactive 2

The effect of contact time was evaluated at interval times of 10 to 30 minute, initial concentration of 0.25, 0.5 and 1 ppm. The effect of time on dye removal by granular and powder pumice is shown in figure 1 and 2. As indicated in the graph, the maximum removal occurred in the first 10 minute.

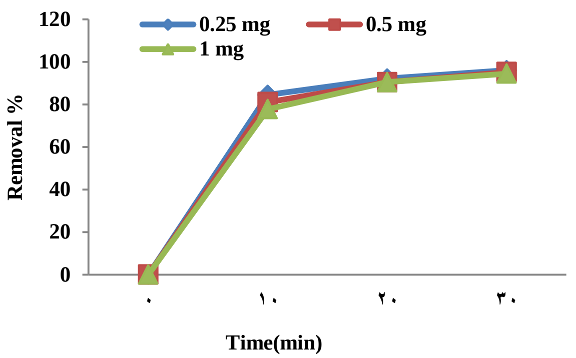


Figure 1) The effect of contact time on dye removal efficiency by powder pumice (pH=3)

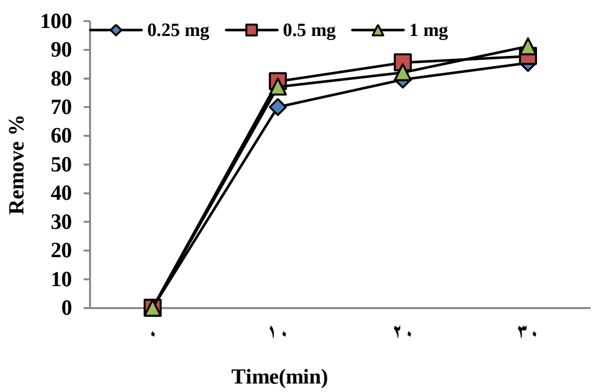


Figure 2) The effect of contact time on dye removal efficiency by granular pumice (pH=3)

The effect of pH

The results of the impact of pH in dye removal by powder and granular pumice are shown in figure 3 and 4. As indicated in the graph, by reducing the pH, dye removal efficiency by powder and granular pumice increased.

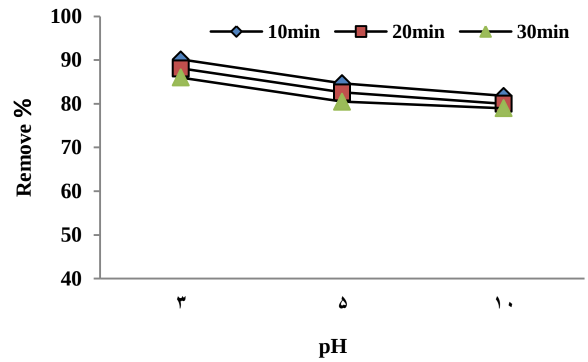


Figure 3) The effect of initial pH of dye solution on removal efficiency by powder pumice

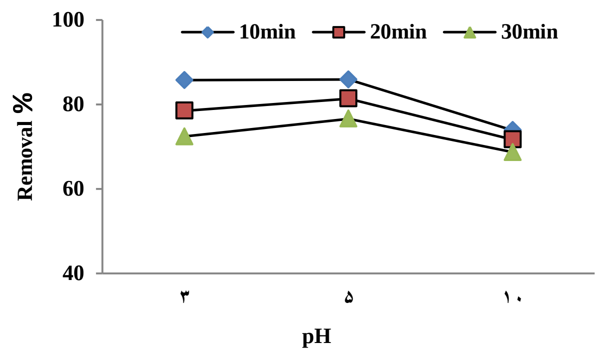


Figure 4) The effect of initial pH of dye solution on removal efficiency by granular pumice

The effect of initial dye concentration

Results showed that by increasing the initial dye concentration from 0.25 to 1 ppm, dye removal efficiency with powder and granular pumice has increased. Figure 5 and 6 show the effect of initial dye concentration on the rate of removal by powder and granular pumice at pH=3 and 30 minute.

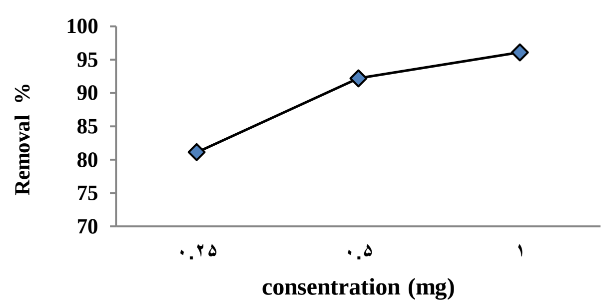


Figure 5) The effect of initial dye concentration on dye removal efficiency by powder pumice at pH=3 and 30 minute.

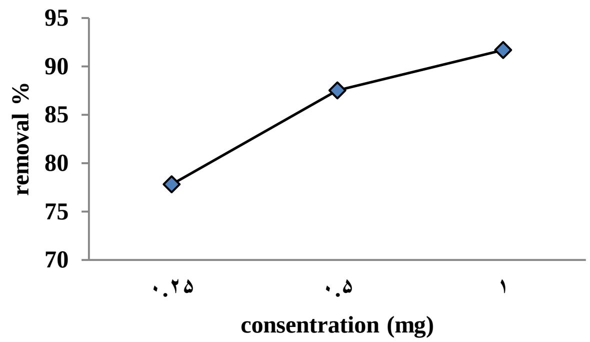


Figure 6) The effect of initial dye concentration on dye removal efficiency by granular pumice at pH=3 and 30 minute.

Adsorption isotherm

Langmuir and freundlich isotherm models are shown to study for granular pumice in Table 3. Determine coefficient value of red reactive 2 adsorption for granular pumice in Langmuir and freundlich models were 0.721 and 0.727, respectively. According to the adsorption process value, it obeys the adsorption isotherm.

Table 3) Langmuir and freundlich isotherm models for granular pumice

Langmuir		freundlich	
Q_0	0.024	K_f	0.024
b	231	n	23
R_L	0.004523	1/n	0.043478
R^2	0.721	R^2	0.727

Also, Langmuir and freundlich isotherm models are shown to study for powder pumice in Table 4. The ion adsorption coefficient value of red reactive 2 for powder pumice in Longmuir and Freundlich models were 0.73 and 0.614, respectively. According to the adsorption process values, it obeys the Freundlich adsorption isotherm more than Langmuir.

Table 4) Langmuir and freundlich isotherm models for powder pumice

Langmuir		freundlich	
Q_0	0.023	K_f	0.019
b	546	n	22.28
R_L	0.719146	1/n	0.044883
R^2	0.733	R^2	0.614

Discussion

The results showed that the main component of pumice structure is quartz with SiO_2 formula that makes up about 74% of it. Presence of this metal oxides in aqueous solutions, cause formation of surface group that are more effective in the contaminant removal of water (19,20). In the studies which had been conducted by Iqbal et al (15), kitis et al (10) and Heibati (21), the main component of pumice structure was Sio_2. This properties enhances the selective adsorption characteristics of porous pumice less than the screw contact time which can be effective on adsorption processes. For a fixed concentration of reactive dyes with a fixed adsorbent mass, the most retention reactive dyes adsorption was in the first 10 minute. Figure 1 and 2 show that, the adsorption rate initially increased rapidly, and the optimal removal efficiencies were reached 10 min: 95.27% and 96.93% for powder and granular pumice, respectively. In other studies, similar results were presented (22-24).

Solution of pH is one of the most critical parameters in the adsorption process and pollutants removal from aqueous solutions (25-27). The effects of initial pH on the adsorption percentages of dyes were researched over a range of pH values from 3, 5 & 10. As elucidated in figure 3 and 4, the maximum dye removal ratios were at the initial pH 3.The results showed that, increasing of pH had decreased the removal efficiency of dye. The best removal percentage obtained at pH 3, were 95.27 and 96.93%, respectively. Obtained results at optimum pH values of adsorbent are in good agreement with the values given in literatures such as walnut shell, sawdust, clay, bentonite, native strains (26,28). In the other studies,similar results were presented (18).

Sorbent dosage has been considered to determine the optimum condition for the performance of adsorption. The removal efficiency of dyes changed with an increase pumice powder and granular dosage from 0. 5 to 1.5 g/100 mL. The adsorption ratios of dyes increased from 67.75 to 95.27%, and from 87.93 to 96.93%, respectively. The removal efficiency of dyes increased with increasing the adsorbent mass which can be attributed to increased surface area and availability of more adsorption sites (29). Also, by comparison of two types of pumice, we can concluded that, the adsorption by powder adsorbent is better than the granules. The reason of this difference could be related to the greater levels of adsorbent in the physical form of powder. The conclusion of this study is the same with Iqbal Fryal (30) and Zarabies (31) studies.

As shown in figure 5 and 6, when the dye concentration was increased from 0.25 to 1 mg/L, the percentages of dyes adsorption increased. So, the equilibrium sorption capacity of the biomass increased with a rise in the initial dyes concentration that this increase in adsorption capacity may be due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher dyes concentration (27,32). In fact, because of the fixed amount of adsorbent and absorbed positions available, by increasing the initial concentration of dye, removal is increased too. Increasing of adsorption capacity occur as a result of the increased mass transfer (27). These results are similar to the results which had been obtained by Yari et al in a study about the removal of reactive dyes (Green, Orange, and Yellow) from aqueous solutions by peanut shell, and application of H_2O_2 and H_2O_2/Fe^0 in removal of Acid Red 18 dye with decreasing pH adsorbent sites due to electrostatic attraction tends to absorb color (32,33). In 2015, Yari et al were investigated removal of Acid orange 2 dye on eggshells. The results of this study revealed that, by increasing the initial concentration of pollutant, the rate of adsorption is reduced (34).

The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature; so, they are fundamentally important in the design of sorption systems (35). The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. Results of Tanyidizi study on reactive black 5 removal with peanut hull showed, the Langmuir model exhibited fits better to the adsorption data than the Freundlich model (36).

The presence of a large number of smaller particles with a larger surface area available for adsorption systems provides for the removal of dyes (35). The amount of dye adsorbed, increased 16% for a decrease in adsorbent particle size. The higher adsorption with smaller adsorbate particles could be attributed to the fact that, the smaller particles provided a larger surface area. The result showed, there was a gradual increase of adsorption with the decrease in particle size. These results are similar to the results which had been obtained by Mahvi et al in a study about the application of acaciatortilis shuck as a low-cost adsorbent to removal of azo dyes Reactive Red 198 and Blue 19, whereas the particle size of the adsorbent as an important parameter in the adsorption of dyes studied (37).

Conclusion

This study has demonstrated that, pumice can be used as an effective adsorbent for Red Reactive 2 dye removal from aqueous solutions. The adsorbent, which was prepared in this study, was cheap and effeceient in removal of red reactive 2 dye than other adsorbents. Results also indicate that, the Red Reactive 2 dye adsorption reaches maximum in pH=3, then decreases with further increase in pH. The results of these isothermal studies showed, the Red Reactive 2 dye removal follows the Freundlich isotherm model (R^2>0.72). The results of this study demonstrated that, the pumice can be used ascheap, highly effective and easy available adsorbent for removal of Red Reactive 2 dye from aqueous solutions.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

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