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Using Natural Stone Pumice in Van Region on Adsorption of Some Textile Dyes

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Abstract: Toxic effect of textile dyes their increasing quantities in air, soil and water environments, because of growing of industrial activities, they must be taken into consideration since they give harm to the environment. We come across textile dyes in natural wetlands as result of uncontrolled industrial wastes. Textile dyes that can accumulate easily in their environments may show toxic effects. Pumice, accruing as a result of volcanic events and durable against chemical factors, is a rock that has porous structure. Pumices have a porous structure because of sudden cooling of the rock and sudden leaving of gases a result of volcanic events. Thanks to these pores, pumices' heat and sound insulation are quite high. The most distinctive feature of pumice from other rocks is that it has different colors and there is not crystal water in its porous structure. Adsorption studies are applied with Van Pumice at pH = 6, the adsorption mechanism and changing dye concentration. As result of these researches, it has been found out that there are different adsorption movements at pH 6 between Neutral Red and Van Pumice. The result of this study shows that the Pumice found in Lake Van gives a better fit for the Langmuir Isotherm (model) and the amount of adsorption increases with the temperature. We thereby conclude that the Pumice located in Lake Van is a recommended adsorbent for filtering the used textile dye in aqueous medium.

Keywords: Textile dyes; adsorption; isotherm; Van pumice; thermodynamics.

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INTRODUCTION

Pumice is a glassy, porous, and volcanic rock which occurs with the result of hollow, spongy, volcanic rocks and is resistant against the physical and chemical effects (22). The name "Ponza" or "Pomza" comes from Italian. There are different names in different languages. In French it is called as "Ponce", in English, the middle ones are "Pumice", naturally the tiny ones are "Pumicite", In German, the big ones are called as "Bimstein", and tiny ones are called as "Bims". In Turkish, it is known as "Sünger taşı", "Köpük taşı", "Topuktaşı" (6).

Because pumice it mostly porous, its heat and sound insulation is quite high. According to Mohs scale, its hardness is 5-6. It does not contain crystal water. Its chemical component; 60%-70% SiO_2, 13%-15% Al_2O_3, 1%-4% Fe_2O_3, 1%-2% CaO, 1%-2% MgO, 2%-5% Na_2O, 3%-4% K_2O and it contains TiO_2, SO_3 and Cl (13, 24).

During formation, because of sudden cooling and the gases inside the pumice's leaving, it contains countless pores from macro scale to micro scale. Between pores are generally (especially micro ones) disconnected hollows. Pores on pumice are mostly not connected to each other. Each pore is isolated from each other with a glassy membrane. Because of this feature, pumice is a good adsorbent (24, 3).

Pores on pumice are smaller than 1 mm. Pores are irregular, spherical, round and like elongated pipes (11, 2).

The more pumice's piece size increases the more porous percent increases. Pumice's excess of porous percent and low specific weight ensure it to be used as a pouring material for insulation areas. Also, thanks to the same features, it is highly porous; Pumice pieces are not too much resistant. However, its durability is suitable for rock durability which was used in carrier wall construction. (To 6 floors). Pumice is a good heat insulator. This feature is increased with the event, which is called as "stack Porousness", in pumice block manufacture that is especially struggled to reach. For the stack porousness, concrete is prepared with a quite thin mortar and is ensured to cover only surround of pumice pieces in a thin manner. The Pumice pores are not only helpful for insulation but also pumice structure elements are highly adsorbent because it has features of removing capillary. Pumice is grinded easily because of being a volcanic glass. Granulated Pumice was used for similar goals both for the purpose of polishing and stoning and in match factories as an ignition material and filling material, soap and cosmetic industry (21, 26).

Because of porous being disconnected and having spaces, pumice is light, it can swim for a long time and its permeability is low and its insulation (heat – sound insulation) is quite high. Chemically, it contains about 75% silica. The amount of SiO_2 that rock contains, provides an abrasive feature to the rock, therefore, it reveals a chemical status that can easily erode steel. The compound of Al_2O_3 provides a high resistant to fire and heat. Na_2O and K_2O are known as minerals which give reactions in textile industry (9).

Economically functioned reserves are generally after tertiary reserves. World's pumice reserves are more than 16 billion tonnes. USA has the biggest reserves while Turkey is the second in terms of total pumice reserves. Important reserves of Turkey are in Tatvan and Ahlat, Niğde-Nevşehir, Iğdır and Kars, Mollakasım (Van), Erciş (Van), Güdül (Ankara), Doğubeyazıt (Ağrı) and Cumaovası' (İzmir).

Main manufacturers are Italy, Greece, Spain, Turkey, France, and Germany (26, 8).

Pumice rocks have recently gained updating as a popular industrial row material parallel to various industries' establishment and development. Pumice was used in a large area mainly as a light structure material, cement production, and filter material, acoustic and polishing in industry. However, in our country, it is mostly used in bleaching jeans and in production of briquette as a light structural material (24, 16).

Coloring of objects is expressed as "dyeing". Dye was used to protect the surface of objects from external influences and to give a nice view. In speech, dye and dye material words are used in the place of each other. These two words are not synonyms. Dyes are generally inorganic. They are mixtures, which are mixed with a connector but dissolved in the medium. They can be removed by scoping in large forms.

The materials which are used to color fabric and fiber are called as "dyeing material" However, all colorful materials or color giving materials are not dye materials. Coloring, applied by dye materials are not similar to coloring, applied by dye. Coloring is generally applied with various dye methods in the form of solution or suspension.

All dye materials are organic compounds. The material to be dyed changes its structure by chemical interaction with the dye. For this reason, the applicant cannot bring the material back to the original by washing or cleaning. For that reason, the first dyes that are used are mixture of metal–oxide, clay and some plant's sap (19).

Fe_2O_3, Cr_2O_3, Pb_3O_4, HgS, graphite can be given as examples for the natural inorganic dyes. Some of the dye materials are from natural sources, and some of them are synthetic. Natural dye materials can be obtained generally from skin of animals and glands, root, shell, seed, and fruit of plants and from microorganisms like yeast bacteria in the result of simple chemical applications (4).

In the textile industry, one of the main problems is the removal of dyes and pigments from the wastewater. It is known that most dyes are toxic, carcinogenic, and mutagenic to aquatic organisms, so they have to be removed. Several methods, such as filtration, coagulation, chemical oxidation, adsorption, *etc*., are used in order to remove dyes from wastewater (18, 23, 9).

One of our aims is to evaluate pumice of the local resource, Van (Turkey), the original material for production of adsorbent. Besides, it is known that pumice has pores. The second purpose of this study is to investigate the adsorption isotherm, kinetics and the thermodynamic parameters adsorption onto pumice derived from the Van region.

MATERIALS AND METHODS

Chemical Materials: Experimental data are obtained from pH=6 solution. Different concentrations of dye material's solution (50 ppm, 60 ppm, 70 ppm) are prepared for the experiment.

Adsorbents: Van Pumice was used as an adsorbent during experiment. Chemical component of this pumice given in Table 1.

Table 1. Chemical components of Van pumice.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss of Combustion
Van Pumice	69.00	14.65	2.51	1.11	0.55	3.520	2.48	0.40	4.76

Method: In this study, Van Pumice was used whose chemical analysis results are given. Adsorption studies were applied with Van Pumice.

Pumices were applied the following operations detailed below:
a) Washing stage: Van Pumice which was grinded in the mill and which was filtered from 230 mesh sieve, was dried for 5.5 hours in the oven. 100 grams of Van Pumice was mixed 12 hours with 1.7 liter of pure water in the mixer. After mixing stage was finished, the material was kept idle for 12 hours. It was observed that aqueous phase and solid phase

were separated. Solid phase was separated by filtering. Solid phase was kept at ambient conditions for 168 hours to dry. Dried Van pumice was filtered again with 230 mesh sieve. It was placed in a desiccator until the time of experiment. Van Pumice was grinded in the mill. After that, the size of the piece was minimized by filtrating 230 mesh sieves.

In the studies of adsorption balance, 1 gram of Pumice was treated 500 mL of dye material solution. Dyeing material solutions were prepared in 50, 60, and 70 ppm concentrations, were shaken with Van Pumice at different times (2, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150, and 180 minutes) in 25 ^{0}C, 35 ^{0}C, 45 ^{0}C temperatures.

Dyeing material adsorption was examined depending on heat and time in the example of Van Pumice. All of the adsorption measurement was applied with a spectrophotometer (T80+ UV/VIS).

RESULTS AND DISCUSSION

Freundlich Isotherm

The Freundlich isotherm assumes an empirical equation based on the heterogeneous surface of adsorbent. The linear form of the Freundlich isotherm is expressed as (15):

$$\log q_e = \log K_f + n \log C_e \quad (1)$$

where K_f is the Freundlich coefficient related to adsorption capacity, and n relates to adsorption intensity. The values of the Freundlich constants were obtained from the linear correlations between the values of log q_e and log C_e. In the Freundlich adsorption constant, n should be greater than 1.

Langmuir Isotherm

In the solid/liquid adsorption process, adsorption of the solute is usually characterized by either mass transfer (boundary layer diffusion) or intraparticle diffusion or even both (12). The adsorption data of dye removal from pumice was analyzed by the Freundlich and Langmuir isotherm models. The Langmuir isotherm model is valid for monolayer adsorption. The linear equation of the Langmuir isotherm is (10):

$$\frac{C_e}{q_e} = \frac{1}{b \times q_m} + \frac{1}{q_m} C_e \quad (2)$$

where, C_e is the equilibrium concentration of dye in the solution, q_e amount of dye adsorbed at equilibrium, q_m Langmuir adsorption capacity, and b Langmuir constant.

The values of the Langmuir constants and coefficient determination R^2 are given in Table 2. The Langmuir adsorption capacity (q_m) was found to be 27.3393, 26.5741 and 23.8115 mg/g at different temperatures (298, 308 and 318 K).

Table 2. Equal values of Neutral Red adsorption on Langmuir and Freundlich equals from different temperature.

T (K)	Langmuir			Freundlich		
	b (L/mg)	q_m (mg/g)	R^2	n	K_f (mg/g)	R^2
298	1,2921	27,3393	0,9997	3,7312	2,5977	0,9997
308	1,0537	26,5741	0,9971	10,0387	3,5430	0,9299
318	1,0209	23,8115	0,9990	34,4567	3,7676	0,7050

When R^2 values of both two adsorption isotherm models are taken into consideration, it shows that the adsorption process has better compliance with the Langmuir adsorption model than the Freundlich model. The Langmuir isotherm model is mostly valid for one layer adsorption over specific number of similar surfaces. If the molecular interaction is neglected, then it can be defined as adsorption behavior of a completely homogeneous surface area. Despite the heterogeneity of the surface, Freundlich-type adsorption isotherm displays the homogeneity of a Langmuir-type adsorption surface. The adsorption of Langmuir isotherm increases linearly together with initial concentration of the adsorbate. At maximum saturation point, the surface is coated with one layer and the amount of adsorbate on the surface remains constant. Also, in this isotherm, the adsorption energy is uniform. The speed of adsorption is directly proportional to the adsorbate concentration and the active places over the surface. The speed of desorption is directly proportionate to the amount of adsorbate adsorbed on the surface.

Thermodynamic Parameters

The thermodynamic parameters such as standard Gibbs fee energy (ΔG), entropy change (ΔS) and enthalpy (ΔH) were calculated using following equations (17, 5):

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (3)$$

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where K_d is the equilibrium constant, C_0 initial concentration (mg/dm^3), C_e equilibrium concentration, V volume (cm^3), m of the pumice (g), T (Kelvin), and R gas constant (8.314 J/mol). The changes in enthalpy (ΔH) and entropy (ΔS) were determined from the slope and intercept of the plots of lnK_d versus 1/T. The Gibbs free energy (ΔG) was calculated using Eq (5).

Table 3. Thermodynamic parameters of Neutral Red adsorption on Van Pumice.

Temp (K)	K_c	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, $kJmol^{-1}K^{-1}$
298	2,6502	-2414,6987		
308	7,5660	-5182,0370	0,0013	0,0292
318	8,4715	-5649,1358		

Concerning the adsorption of Neutral Red solutions onto the Pumice found in Lake Van, thermodynamic parameters such as ΔG, ΔS and ΔH were determined at temperatures of 298, 308, and 318 K.

The negative value of Gibbs free energy (ΔG) shows that the adsorption process of Neutral Red onto the Pumice located in Lake Van is spontaneous. The (ΔG) value tends to decrease at increasing temperatures and thus demonstrates that this process can be carried out much easier at high temperatures. The positive value of ΔS shows that, at the interface between Neutral Red solution and the Pumice found in Lake Van, the sorption process tends toward increasing disorder. The positive value of ΔH points out that the sorption process is endothermic.

Adsorption Kinetics

The experimental data relating to adsorption of dye onto pumice was investigated using the Lagergren pseudo-first and pseudo-second order equation (1, 7):

$$log(Q_e - Q_t) = log(Q_e) - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2} + \frac{1}{q_e} t \quad (7)$$

where, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t amount of dye adsorbed at various times, t time of adsorption duration, and k_1 is a rate constant of the equation (min^{-1}).

The k_1 and q_e were calculated from the slope and intercept of the plots of log (q_e – q_t) versus t according to the pseudo-first-order model (Fig. 1) and t/q_t versus t according to the pseudo-second-order model (Fig. 2) as well as q_e and k_2 from the slope and intercept were calculated.

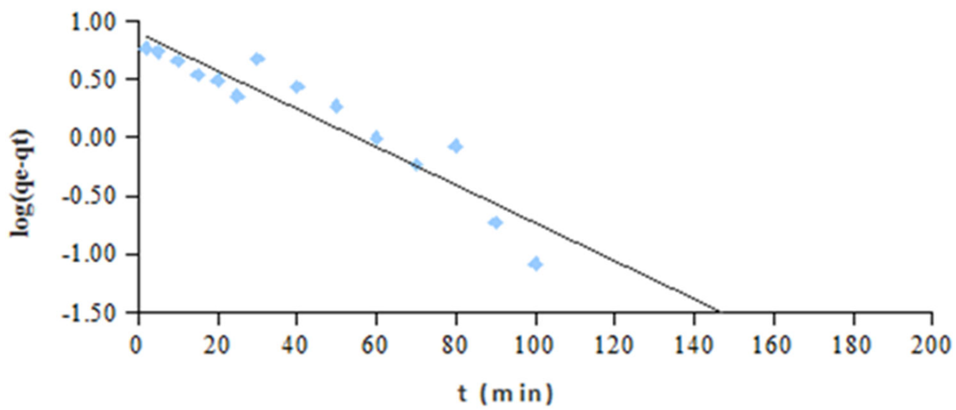

Figure 1: Pseudo first order graph of Dye Adsorption on Van Pumice.

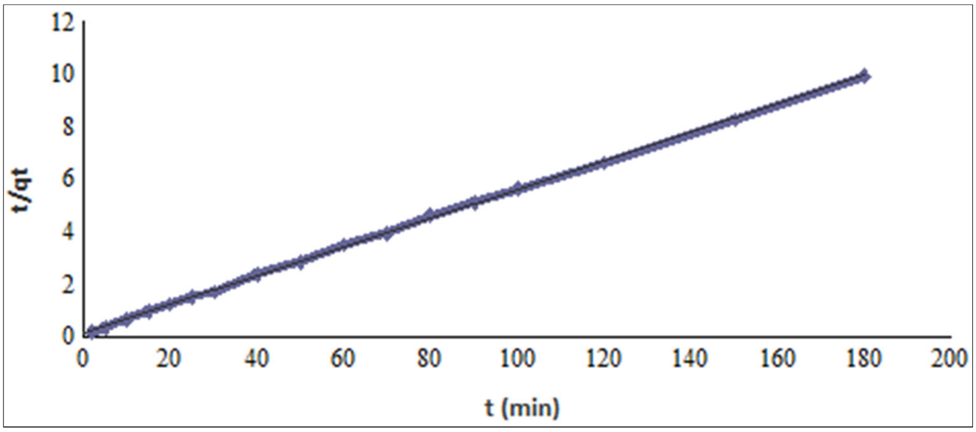

Figure 2: Pseudo second order graph of Dye Adsorption on Van Pumice

Table 4. Pseudo first order parameters of the dye.

T (K)	k_1	q_e (calc.)	q_e (exp.)	R^2
298	0,0215	2,7455	18,1510	0,7089
308	0,0374	7,8126	22,0815	0,8870
318	0,0357	3,0300	22,3605	0,7560

Table 5. Pseudo second order parameters of the dye.

T (K)	k_2	q_e (calc.)	q_e (exp.)	R^2
298	0,0250	18,2929	18,1510	0,9995
308	0,0115	22,5745	22,0815	0,9987
318	0,0388	22,5004	22,3605	0,9998

Regarding all the initial pumice amounts and temperature values of pumice, we concluded that the kinetics of sorption onto the pumice has indicated a good compliance with the quadratic form of the kinetic model. The correlation factor R^2 was found above 0,99.

CONCLUSION

Considering all these results, we have concluded that the Pumice found in Lake Van is a recommended adsorbent for the used dyestuff. We consider that the Pumice found in Lake Van which is currently used in many fields of application, can also be used as an adsorbent.

In his Master of science thesis, "BIOSORPTION OF VICTORIA BLUE R (VBR) ONTO IMMOBILIZED BIOMASS OF BONE CHAR AND SUNFLOWER HUSK", Ozdemir has applied his experimental data to the Langmuir isotherm model and obtained the resulting R2 values at different temperatures, varying between 0,974 and 0,989. He later found out that these high regression coefficients and its biosorption have indicated good compliance with the Langmuir isotherm. Compliance with Langmuir isotherm showed out that the biosorption occured on homogenous surfaces and the dye material VMR has coated the KIKU, forming only one layer (20).

In his master of science thesis "Removal of Dye Materials from Aqueous solutions by Adsorption on Coals and Cokes", Kayacan has observed that both types of cokes comply with the Freundlich isotherm and also with the Langmuir isotherms at the same time. Besides, the MKP cokes rather comply with the Langmuir isotherm and the DB cokes comply with Freundlich isotherm. It is thereby concluded that the MKP cokes have relatively homogenous surfaces, but on the other hand, the DB cokes have relatively heterogeneous surface. He found out that the b values of Langmuir's isotherm of MKP cokes were relatively high, thus he concluded that this is a clear proof of why these cokes are good adsorbents (14). It is clear that both studies support our study.

In their studies, Turkmenoglu and her friends have used acidic Pumice found in Lake Van in sizes of 0-2 mm, 2-4 mm and 4-8 mm respectively. They have found the physical features of Pumice found in Lake Van as follows (25):

Van Pumice	0-2 mm	2-4 mm	4-8 mm
Specific Weight Factor	1,72	1,32	1,06
Water Absorption Rate (%)	-	36,71	38,83
Bulk Density (kg/m^3)	636	495	413

The chemical and physical features of Pumice are some of those determining factors to find out if it is a good adsorbent or not.

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