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Investigation of the Usability of Perlite Waste for Dyestuff Removal from Aqueous Solution

Uğur Selengil[1], Tijen Ennil Bektaş*[2]

Abstract

In this study, unexpended perlite waste obtained from a factory producing expanded perlite was used as adsorbent. Malachite green (MG), which is a cationic dyestuff, was used as adsorbed material. The pore properties including the BET surface area, pore volume and average pore diameter were characterized. The chemical composition of the perlite was analysed by XRF. The effects of initial pH, the amount of adsorbent, contact time and initial dyestuff concentration were examined. The adsorption kinetics of dyestuff obeys the pseudo second-order kinetic model. The experimental data indicated that the adsorption isotherms are well described by the Langmuir isotherm equation. 99% dyestuff removal was obtained under optimum conditions. As a result, it was found that perlite waste was a suitable adsorbent for malachite green dyestuff.

Keywords: Perlite waste, dyestuff, adsorption, isotherm

1. INTRODUCTION

Wastewaters contain organic and inorganic pollutants. Organic pollutants include pesticides, phenolic and dyestuffs. Dyestuffs are often of synthetic origin and are more stable and more difficult to biodegrade complex consists of aromatic molecular structures. Dyestuffs are usually very intense and bright colors. They are visible even if they are of very low concentration (less than 1 mg/L). Due to the chemical structure of dyes and their resistance to light and oxidation, dyestuffs are very difficult to biodegrade in environment [1]. Therefore, dyestuff removal from wastewater is necessary for human and environmental health. Colored wastewater is usually treated by physical or chemical processes. These methods include coagulation / flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and adsorption processes. Adsorption has been widely used and an attractive method for the removal of dyestuff from wastewaters. Activated carbon is the most widely

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used adsorbent in adsorption due to its high porosity. However, activated carbon is more expensive than other adsorbent materials and the price increases as the quality increases. For this, most researchers have made studies to find a cheaper, abundant and efficient alternative substance. Adsorbents such as fly ash [2], zeolite (226.7 mg/g, 43.29 mg/g) [3, 4], sepiolite [5], bentonite (7.7 mg/g)[6, 7], plant roots (42.6 mg/g) [8], tree bark [9], chitosan [10] were used for dyestuff removal.

Perlite is a general name given to naturally occurring silicaous volcanic stones that can be found all over the world. A unique feature of perlite is that it can expand up to 30 times its original volume when heated to a temperature of 750–1200 ºC. Perlite is important with its low density in small volume, physical flexibility, chemical stability, low sound permeability, fire resistance. Perlite is used in many industries such as construction, agriculture, food, pharmaceutical, thermal insulation. As a result of the sudden heating of the ground perlite, the expanded light material is stored in the silos as a top stream of the vertical furnace with the help of vacuum. The waste material that is not affected by the sudden high temperature reached in the ore is taken as vertical furnace downstream and stored in big sacks.

In this study, unexpended perlite waste obtained from a factory producing expanded perlite was used as adsorbent. The objective of the present study was to perlite for the removal of malachite green (MG) from aqueous solutions. Toward this aim, the effects of contact time, pH, adsorbent dosage, temperature and initial concentration, on the adsorption of MG were investigated. The Langmuir and Freundlich isotherm models were tested for their applicability. The experimental data were analyzed using the pseudo first-order, pseudo second-order, and intraparticle models, and kinetic constants were evaluated.

2. MATERIALS AND METHODS

In this study, perlite waste obtained from a company producing expanded perlite was used as adsorbent. In this study, perlite waste with a grain size of 95.8% under the sieve 0.080 mm (80µm) was used in adsorption experiments. The sample contains approximately 1% moisture. The specific surface area of the perlit particles was measured by the BET nitrogen gas sorption method. In order to measure nitrogen gas adsorption (77 K), Quantachrome, Autosorb 1C device was used. The Brunauer–Emmett–Teller (BET) equation was utilized for the calculation of the BET surface area from N_2 adsorption data. The chemical composition of the perlite was analysed by XRF. The results are given in Tables 1 and 2.

Table 1. Characteristics of the perlit

BET surface area (m^2/g)	12.93
Micropore area (m^2/g)	3.912
Total pore volume (cm^3/g)	0.01999
Micropore volume (cm^3/g)	0.00139
Mesopore volume (cm^3/g)	0.0186
Average pore diameter (nm)	6.183

Table 2. Chemical analysis of perlite

SiO_2	**Al_2O_3**	**TiO_2**	**CaO**	**MgO**
73.8	14.1	0.129	1.24	0.291
Na_2O	**K_2O**	**SO_3**	**Fe_2O_3**	**LOI**
2.63	5.86	0.08	1.55	4.24

LOI: loss on ignition.

Malachite green oxalate was purchased from Merck. The malachite green oxalate is a basic and cationic dyestuff; molecular formula $C_{52}H_{54}N_4O_{12}$, chemical formula $C_{46}H_{50}N_4.2C_2HO_4.C_2H_2O_4$ (Fig. 1). Different concentrations of malachite green oxalate were prepared from a stock of 1000 mg/L solution.

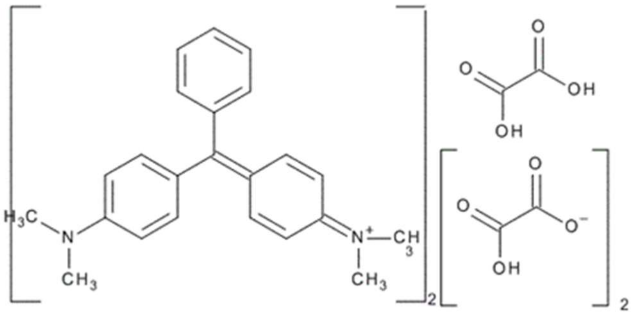

Figure 1. Malachite green oxalate

A certain amount of adsorbent was added to a certain volume of dyestuff solution and kept in a shaking water bath for 24 hours. The effect of pH on malachite green adsorption was investigated for three different initial concentrations of malachite green (100, 250 and 500 mg/L). The pH values of the samples were adjusted with NaOH and HCl solutions at various pH values. Initial concentrations of 100 mg/L, 50 mL of dyestuff solution were prepared at the original pH (3.54) and pH 6 values. 0.1 - 1.0 g perlite waste was added to each flask and kept in a shaking water bath with a temperature of 25 ºC for 24 hours. To examine the effect of contact time and kinetic models, the solution and the adsorbent were kept in the shaking water bath at different time intervals. Dyestuff solutions ranging from 50-750 mg/L were prepared to examine the effect of initial concentration on dye removal. The pH was adjusted to 6. 0.2 g of perlite waste was added and left in the shaking water bath for 5 hours at 25 ºC and 45 ºC for isotherm studies.

All concentrations were measured at 617 nm, that corresponds to maximum absorbance, using a spectrophotometer (Shimadzu UV-120-01).

3. RESULTS AND DISCUSSION

3.1. Effect of Initial pH

The effect of pH on malachite green adsorption was investigated for three different initial concentrations of malachite green (100, 250 and 500 mg/L). 0.5 g of perlite was added to 50 mL of the solution and it was kept in a shaking water bath at 25 ºC for 24 hours. The results are given in Fig. 2.

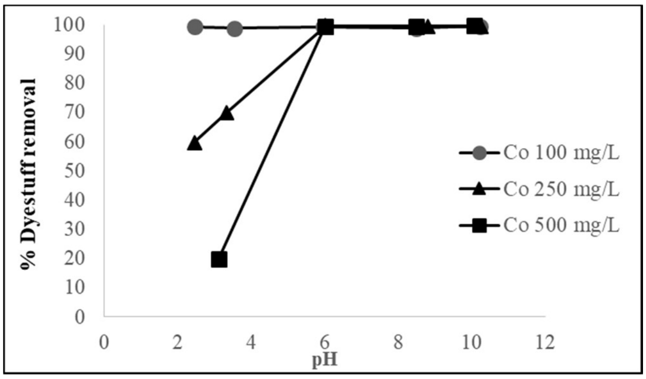

Figure 2. Effect of initial pH on dyestuff adsorption.

As can be seen from the Fig. 2, very high dyestuff removal was obtained for all pH values at 100 mg/L initial concentration. At the initial concentrations of 250 and 500 mg/L, the highest dye removal was observed for pH 6 and greater. Since the surface of perlite is negatively charged at all pH values due to its oxide structure, the positive charged cationic dyestuff molecules are more easily attached to the surface in high pH environments.

3.2. Effect of Adsorbent Amount

In order to examine the effect of adsorbent amount on dyestuff removal, different amounts of perlite (0.1-1 g/50 mL) were added to 100 mg/L solution at original pH and pH 6 and contacted in a shaking water bath at 25 °C for 24 hours. The results are given in Fig. 3.

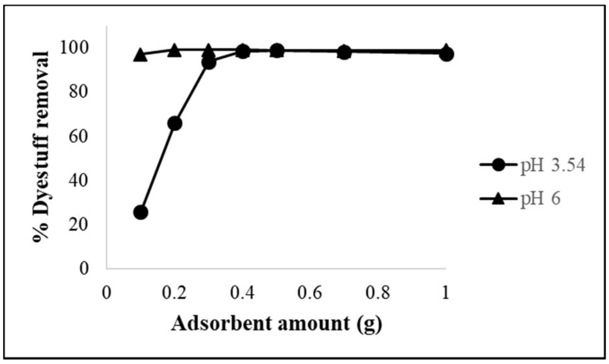

Figure 3. Effect of adsorbent amount on dyestuff adsorption.

According to the results adsorption by increasing the amount of adsorbent at the original pH (3.54). At pH 6, a high removal was obtained for all adsorbent amounts. Therefore, the optimum amount of adsorbent was taken as 0.2 g/50 mL and 0.5 g/50 mL at pH 6 and 3.54, respectively.

3.3. Effect of contact time

Inadequate contact time of the dyestuff and adsorbent may not provide good removal. Therefore, optimal contact time was determined. For this purpose, 100 mg/L solutions at original pH were shaken with 0.5 g perlite at 25°C for different periods. The results are given in Fig. 4.

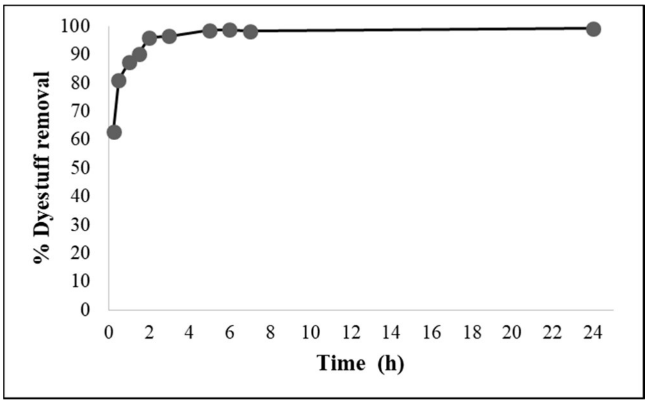

Figure 4. Effect of contact time on dyestuff adsorption.

It was observed that adsorption took place rapidly in the early hours and reached equilibrium after 5 hours.

In order to explain the mechanism of adsorption process, pseudo-first-order, pseudo-second-order kinetic models were examined. The rate constant of pseudo-first-order adsorption is determined from the following equation given by Lagergren [11, 12]:

$$\log(q_e-q_t)=\log q_e-k_1t/2.303 \qquad (1)$$

where, q_e and q_t are the amounts of dyestuff adsorbed (mg/g) at equilibrium and at time t (h), respectively, and k_1 (h^{-1}) is the rate constant of the pseudo-first-order adsorption. Value of k_1 was calculated from the plot of $log(q_e - q_t)$ vs. t for perlite (Fig. 5).

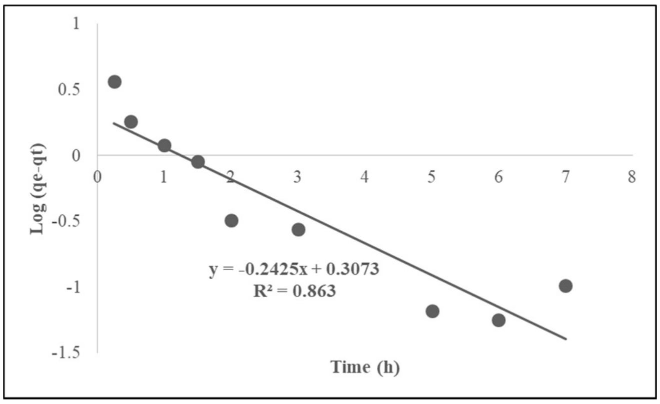

Figure 5. Plot for pseudo-first-order model for dyestuff adsorption by perlite.

The pseudo-second-order equation based on adsorption capacity may be expressed in the form [13, 14]:

$$t/q_t=1/k_2q_e^2+t/q_e \qquad (2)$$

Here k_2 (g/mg h) is the rate constant of pseudo-second-order adsorption. k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t vs. t (Fig.6).

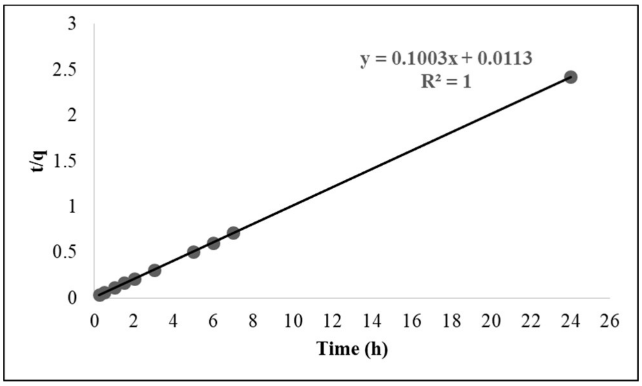

Figure 6. Plot for pseudo-second-order model for dyestuff adsorption by perlite.

Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulate, followed by diffusion of the solute molecules into the pore interiors The intraparticle diffusion equation can be described as [15]

$$q_t=k_it^{1/2}$$

where *ki* is the intraparticle diffusion rate constant (mg/g min$^{1/2}$). The *ki* is the slope of straight line portions of the plot of q_t vs. $t^{1/2}$ (Fig. 7)

The kinetic constants are given in Table 2. The results showed that the pseudo-first-order rate expression and intraparticle model were not valid in the present systems studied. The experimental q_e values did not agree with the calculated ones. The good correlation coefficients for the pseudo-second-order kinetic model can justify the adsorption mechanisms, indicating the chemical adsorption is the rate-limiting step. Also, the calculated q_e values agree very well with the experimental data.

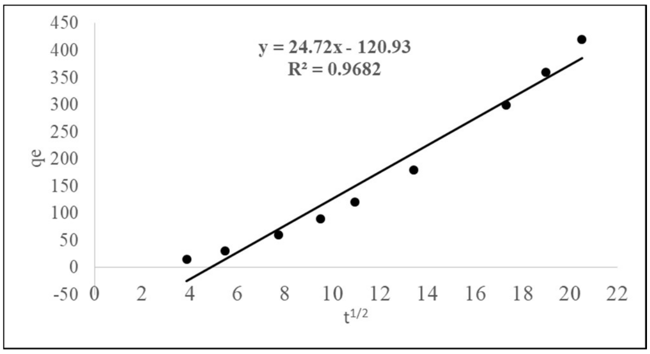

Figure 7. Plot for intraparticle model for dyestuff adsorption by perlite.

Table 2. Kinetic parameters for dyestuff adsorption

q_e (mg/g) (experimental)	Pseudo-first-order			Pseudo-second-order		
	k_1 (h^{-1})	q_e (mg/g)	R^2	k_2 (g/mgh)	q_e (mg/g)	R^2
9.9163	0.5584	2.029	0.86	0.8902	9.9701	1
	Intraparticle model					
	ki (mg/g min$^{1/2}$)			R^2		
	24.72			0.97		

3.4. Effect of initial concentration

The effect of initial dyestuff concentration on removal was investigated. The amount of dyestuff sorbed increased with increased initial concentration. As the concentration of dyestuff in the solution increases, it will be easier to fill the dyestuff molecules into empty centers on the adsorbent surface. The amount of dyestuff sorbed at equilibrium (q_e) increased from 12 to 101 mg/g and from 12 to 121 mg/g as the concentration was increased from 50 to 750 mg/L for 25°C and 45°C, respectively. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dyestuff concentration.

The adsorption isotherms are used to calculate the adsorption mechanism and maximum adsorption capacity. The experimental data were applied to the Langmuir, Freundlich isotherm equations. Eq. 3 is used for Langmuir isotherm [15];

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (3)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of dyestuff adsorbed at equilibrium (mg/g) and b are Langmuir constants related to monolayer sorption capacity and energy of sorption, respectively.

The Freundlich equation is represented by the Equation 4 [15];

$$\ln q_e = \ln K + (1/n) \ln C_e \quad (4)$$

where K (mg/g) is the Freundlich capacity constant and n is the Freundlich intensity constant. A plot of linear Langmuir and Freundlich equation are shown in Fig. 8 and 9.

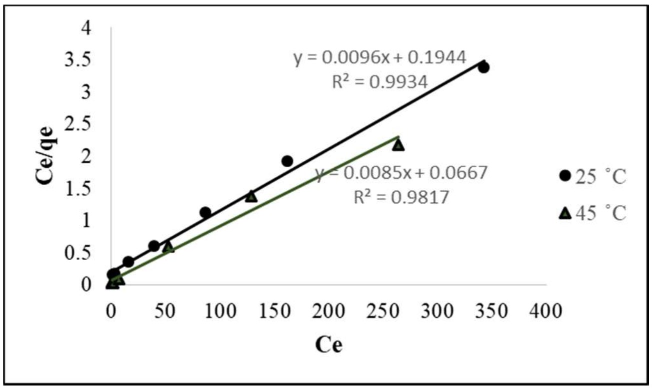

Figure 8. Langmuir isotherm plots for dyestuff removal.

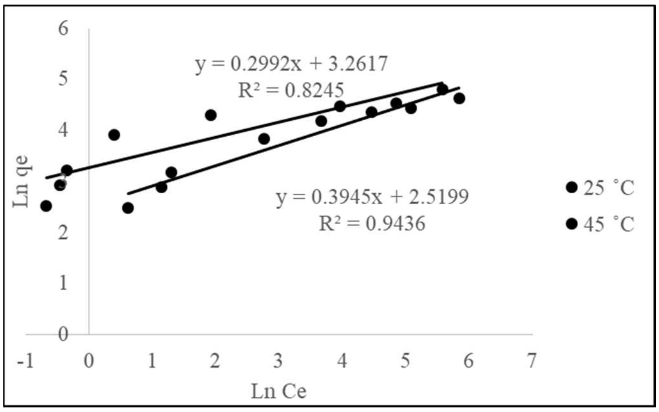

Figure 9. Freundlich isotherm plots for dyestuff removal.

The constants of Langmuir and Freundlich equation were given in Table 3. As we can see, the experimental data are fitted well by Langmuir isotherms with linear regression coefficients greater than 0.98. It can be said that monolayer adsorption occurs on homogeneous surface.

Table 3. Langmuir and Freundlich isotherm constants

	Temperature (°C)	R^2	Qo (mg/g)	b (L/mg)
Langmuir	25	0.9934	104.16	0.049
	45	0.9817	117.64	0.127
		R^2	1/n	K
Freundlich	25	0.9436	0.39	12.42
	45	0.8245	0.29	26.09

4. CONCLUSIONS

In this study, usability of perlite waste in adsorption was investigated. At three different initial concentrations, the dyestuff removal at pH 6 reached 99%. The adsorbent amount increases while the adsorption of dyestuff increases, reaching a plateau value after a certain value for original pH and pH 6. After this plateau, the adsorption event equilibrates and the dye removal does not change as the amount of adsorbent increases. The pseudo-second order kinetic model agrees very well with the experimental data. When the adsorption isotherms were examined according to Langmuir and Freundlich adsorption isotherm models at 25 °C and 45 °C temperatures, it was found that it conforms to Langmuir isotherm model. As a result of this study, it is observed that perlite waste used is suitable for removal of malachite green from wastewater since 99% removal is obtained.

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