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Application of mine waste for wastewater treatment: Efficient organic pollutant removal

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Abstract

In this research, a high porous silicate mining waste that was prepared from Syah Kamar Polymetal Porphyry mine in order to malachite green dye (MG) removal has been applied. The characterization of this natural mineral was determined using the XRD, XRF, SEM and FT-IR analysis. The MG adsorption onto high porous activated waste was studied based on the parameters of pH, temperature, adsorbent dosage, initial dye concentration and contact time. The equilibrium and kinetic adsorption models were experimentally investigated. The obtained data have suggested that the process of MG removal followed up the Sips isotherm and pseudo-second order kinetic. The thermodynamic parameters values consist of ΔG°, ΔH° and ΔS° confirms that the adsorption of MG is spontaneous and exothermic reaction. In the optimal condition the removal of MG was more than 93%. This method has a number of advantages, including being low-cost and non-toxic and the availability of natural adsorbent.

Keywords: *High Porous Silicate, Syah-Kamar Polymetal Porphyry Mine Waste, Malachite Green Dye, Adsorption.*

1. Introduction

In the past few decades, the increasing level of water contamination has caused very serious concerns among environmentalists. The dye and pigment colored chemicals which are discharged from a wide range of industries, in terms of the large-scale production and extensive application, were taken into consideration as one of the most important environmental challenges which facing humankind (Mahmoodi et al. 2016a). Every year, a large amount of wastewater is being produced due to the industrial and domestic activities. The treatment and recycling of wastewater are an unavoidable alternative to compensate for the crisis of water shortage (Hosseini et al. 2016). During the past two decades, in order to address the problem of water contamination, the focus has been on the industries of textile, dyeing, paper-making and other commercial activities (Moussavi and Mahmoudi 2009; Mahdavi-Talarposhti et al. 2001; Yagub et al. 2014; Dang et al. 2016). The presence of even trace amount of dye in water is completely visible (Mahmoodi et al. 2015). Water contamination results in the disorder of the aquatic organism's activity as well as changing the appearance of water (Bailey et al. 2002). More importantly, some synthetic dyes are carcinogenic (Dang et al. 2016). Toxicity and high stability are the most important properties of synthetic dyes which in turn contributes to difficulty in degrading them (Polak et al. 2016).

A basic dye of Triphenylmethane type is Malachite Green (MG) which its discharge in water is followed by undesirable color and the reduction of sunlight penetration. It can consequently, runs a risk for aquatic life even at low percentages because of its carcinogenic, genotoxic, mutagenic and teratogenicity properties (Li et al. 2016). In recent years, according to these concerns, various investigations have been carried out so as to removal of dyes from wastewater. Many methods have been proposed based on these researches, including biological, chemical, biochemical, chemical oxidation, adsorption and membrane filtration which each of them has its own advantages and disadvantages (Moussavi and Mahmoudi 2009; Rehman et al. 2012; Yagub et al. 2014). Adsorption process is one of the most common physical treatment methods of wastewater (Mahmoodi et al. 2016b). It has been proven that adsorption process because of its simplicity, low-cost, ease of operation, flexibility, minimum sludge production and non-sensitivity to toxic compounds, and is the most effective method in comparing with other available methods. For this purpose, many adsorbent including activated carbon and artificial polymers have been studied, but some important problem is associated with these adsorbent like high-cost and not being time-saving. Therefore, adsorbents which are low-cost and have high capacity of adsorption in short time, are preferred (Mahmoodi et al. 2016c). In general, adsorption capacity of adsorbent depends on the surface properties such as surface area and functional groups (Han et al. 2016).

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Adsorption process depends on a number of effective variables including contact time, adsorbent dosage, initial concentration of dye and pH value (Senthamarai et al. 2013; Mahmoodi et al. 2016b). Various types of natural and artificial adsorbents for removal of dye from colored water and wastewater have been studied. Activated carbon has been utilized as one of the most conventional adsorbent for colored wastewater treatment, but due to its high initial cost, the necessity of finding alternative adsorbents with low cost and high adsorption capacity has been considered as a striking issue for researchers. For example about natural adsorbents, Fan et al. (2016) investigated the removal of both cationic malachite green and anionic Congo red dyes using magnetic hydroxyapatite nano powder from aqueous solution (Zhang et al. 2016).

Base on the literature review of the adsorption process that was brought, in this paper high porous silicate mining waste (SMW) that was prepared from Syah Kamar Polymetal Porphyry mine was produce as an adsorbent. Therefore, high porous SMW was used for removal of basic dyes consist of MG dye wastewater in the batch system.

2. Experimental methods

2.1. Preparation of adsorbent

The raw sample of SMW that used in this study, was prepared from Iran Syah Kamar Polymetal Porphyry mine. Firstly, samples crushed with jaw crusher and then washed with double distilled water. After that, samples dried in oven with temperature of 80°C for 2h time. Afterwards, in order to achieving nano size and high fine particles, powder re-crushed by planetary Ball Mill Narva-MPM-250 Model for 2h agitation speed of 600 rpm. Eventually, porous SMW adsorbent was used so as to study the adsorption process.

2.2. Characterization of High Porous SMW Adsorbent

For characterization of high porous SMW adsorbent X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FT-IR) analysis were used. The XRF analysis is shown in Table 1.

According to XRF analysis, Al_2O_3, Fe_2O_3, SiO_2 and K_2O oxides are major compounds of high porous SMW adsorbent. Also, in order to study morphology and particle dimension, the SEM images are used. SEM images are shown in Figure 1, which clearly indicates the high porosity and nano dimensions of particles.

According to Figure 1, as is obvious, high porous SMW adsorbent particles have granular and partially smooth tissue and their size are smaller than 100 nm and this high porous SMW adsorbent have suitable potential be used for wastewater treatment. In Figure 2, the XRD major peaks along with their chemical compounds are shown.

According to Table 1 and Figure 2, it is obvious that the XRF analysis confirmed the XRD spectrum. Base on the XRD spectrum the main peaks concern to feldspar, silica and muscovite silicate minerals. In order to determine natural functions of high porous SMW adsorbent process, the FT-IR spectra were used which its results are shown in Figure 3.

All of the important peaks consist of B1-B7 were interpreted and the concept of these major peaks were showed in Table 2. Among all of the peaks that detected in FT-IR spectra the hydroxyl functional group (OH^-) is an important than others, because of its adsorptive features. Therefore, based on characterization analysis such as XRD, XRF, SEM and FT-IR, the high porous SMW adsorbent can be used for the purpose of wastewater treatment.

2.3. Batch system adsorption experiments

The removal tests have been carried out in volumes of 250 mL of synthetic solution of MG dye.

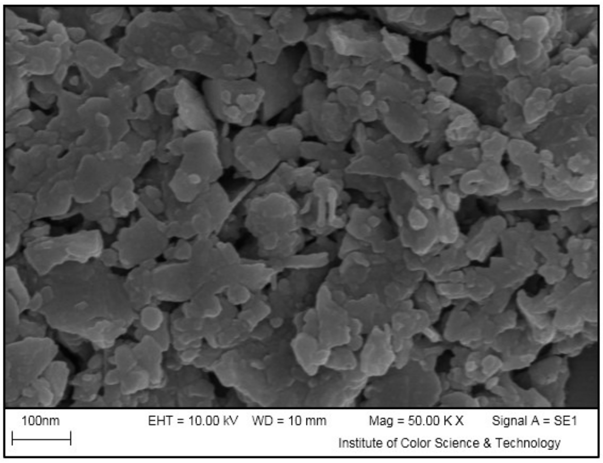

Fig 1. The result of SEM Image of high porous SMW adsorbent.

Table 1. The XRF result of high porous SMW adsorbent.

Analyte	Value (%)
Al_2O_3	48.6224
Fe_2O_3	40.7968
SiO_2	3.9917
Na_2O	3.1078
K_2O	1.4672
CaO	1.2580
ZnO	0.3808
MnO	0.1714
TiO_2	0.1215
P_2O_5	0.0824
MgO	0.0000
Total	**100**

With the exception of those experiments which are studied in order to calculate the amount of parameter, through all tests, solutions with the concentration of 10 mg/L in optimum pH at laboratory temperature, have been utilized.
Studied solution were mixed by Jartest and samples at time intervals of 10, 20, 40, 60, 80 and 100 min were centrifuged for 5 min at 4500 rpm and the concentration of dye was calculated from the measured absorbance in the supernatant at its corresponding maximum adsorption wave length (λ_{max-MG} = 620 nm), by means of an UV spectrophotometer (Unico-2100 model). The concentration of dye was calculated as Eq. 1 (dye removal percentage):

$$\text{Removal (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (1)$$

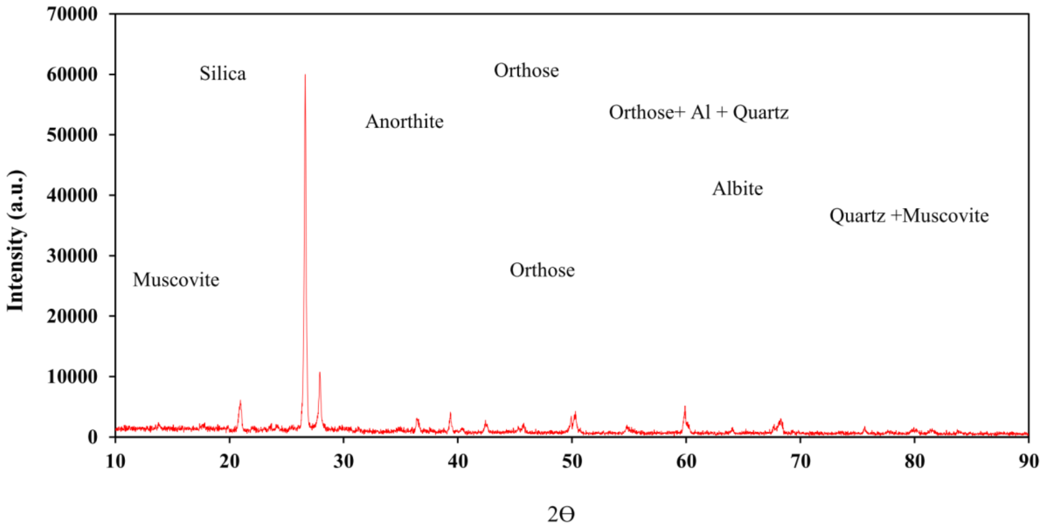

Fig 2. The XRD spectrum of high porous SMW adsorbent.

Table 2. FT-IR spectra peaks and related functional groups of high porous SMW adsorbent.

Band name	Band position in FT-IR spectra (cm^{-1})	Functional group
B1	434.3	Si–O stretching vibrations of Si–O–Si
B2	546	Si–O stretching vibrations of Si–O–Al
B3, B4 and B5	1001, 1464 and 1566	deformation of molecular water
B6	3395	OH^-
B7	3856	H_2O

Where, C_0 and C_t stand for dye initial and final concentration. Also, the amount of adsorbed dye on equilibrium q_e (mg/g) was calculated as Eq. 2:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

Where C_0 and C_e (mg/l) denote for dye initial and equilibrium concentration, V is the volume of the solution (mL) and W is the adsorbent dosage (g). Chemical structure of MG dye is shown in Figure 4.

3. Experimental studies

3.1. Dyes adsorption by high porous SMW adsorbent

Through the study of each parameter of pH, contact time with adsorbent, the amount of adsorbent, the concentration of solution containing and temperature, several amount of each parameter were determined, while other parameters were constant. Then, providing with all suitable conditions, the final amount of adsorption was calculated. Finally, the efficiency of high porous SMW adsorbent was investigated.

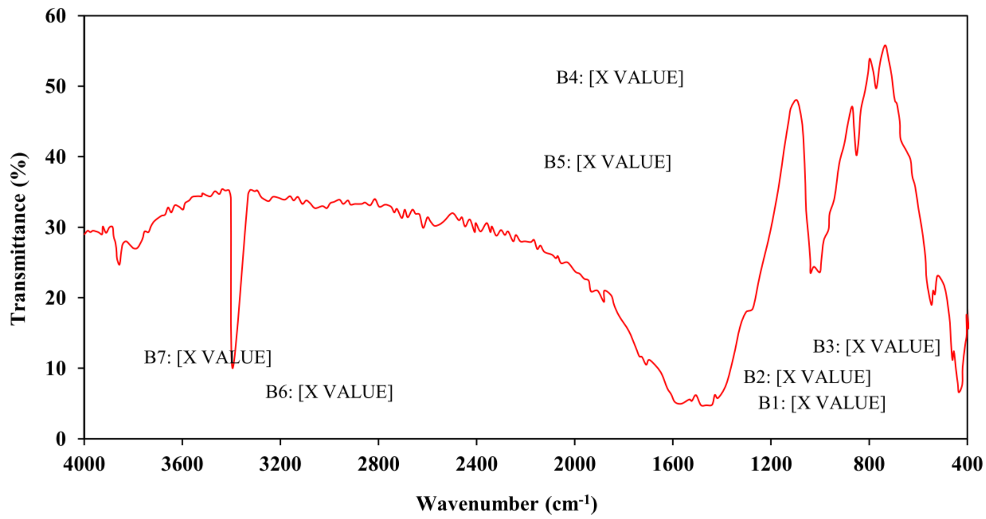

Fig 3. The FT-IR spectra of high porous SMW adsorbent.

3.2. The effect of pH

The solution pH is one of the most influential factors in the process of adsorption. The process of adsorption of MG dye in pH 3, 4, 4.8, 6, 7.5 and 9 with the concentration of 10 mg/L using 0.5 g adsorbent has been assessed. In order the adjust pH, NaOH and HCL 0.1 M solutions were used. The effect of pH on MG dye adsorption using high porous SMW adsorbent is shown in Figure 5. Figure 5 indicated that the efficiency of malachite green dye adsorption has been affected considerably by the pH of the solution. Maximum removal of MG dye occurred in pH 9. Due to degrading the structure of MG dye, higher pH has not been studied.

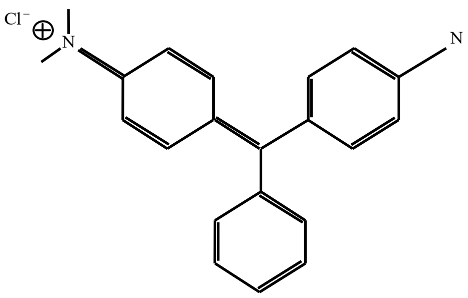

Fig 4. Chemical structure of malachite green dye.

3.3. The effect of adsorbent amount

The dependency of the amount of MG dye adsorption on the weight of high porous SMW adsorbent was investigated. The solution of aqueous MG dye with concentration of 10 mg/L, at temperature of 11 ˚C with agitation speed of 150 rpm and centrifuge of 4000 rpm in 5 min in pH 9, was used. The effect of adsorbent amount on the adsorption of MG dye is shown in Figure 6. With increasing the amount of adsorbent, the percentage of removal has been increased, because of the increasing of adsorption area and adsorptive sites.

3.4. The effect of MG dye concentration

The effect of dye concentration on adsorption process of high porous SMW adsorbent at laboratory temperature with agitation speed of 150 rpm and centrifuge of 4000 rpm in optimum pH has been studied (Fig 7). Figure 7 confirms that with increasing concentration, MG dye adsorption percentage decreases.

3.5. The effect of temperature

The temperature effect on MG dye adsorption, with study of temperature of 284, 298 and 318 K in pH 9 using 0.5 g adsorbent and concentration of 10 mg/L for solution has been assessed. The results of these experiments are shown in Figure 8. After study of temperature, Figure 8 indicates decreasing of equilibrium time as the result of increasing temperature. Although, at higher temperature the adsorption differences are not so sensible, but increasing the amount of MG dye adsorption is completely notable. Hence, it is concluded that increasing temperature has positive impact on adsorption process.

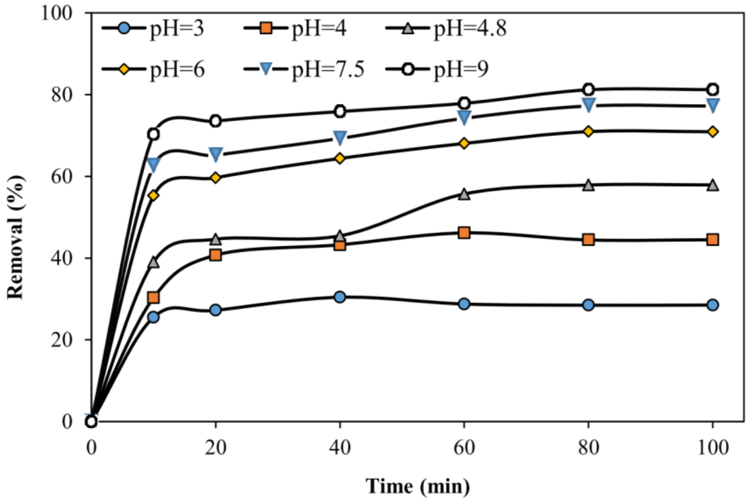

Fig 5. Effect of pH on removal of MG in C_0=10ppm, adsorbent dosage = 0.5g and T = 11˚C.

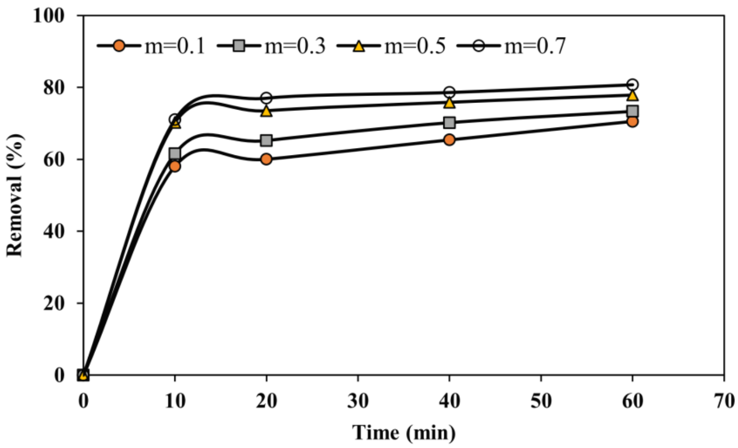

Fig 6. The effect of adsorbent dosage on the removal of MG dye at pH=9, C0=10mg/L and T=11˚C.

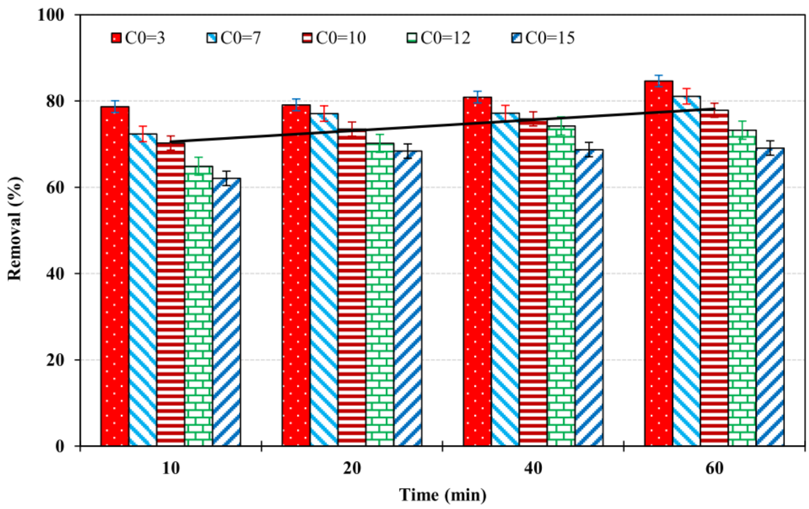

Fig 7. The effect of initial concentration (C_0) change for removal of MG dye at pH=9, adsorbent dosage=0.5g, T=9˚C.

4. Kinetic, thermodynamic and equilibrium studies

4.1. Adsorption equilibrium

To describe adsorption process, isotherm models should be studied. In general, isotherms models provide important information about optimum usage of adsorbent. In this regard the isotherms of Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich (D–RK), Sips and Redlich-Peterson (R–P) have been considered (Seifpanahi-Shabani et al. 2013). The Langmuir isotherm model, assumes that the adsorption occurs at homogeneous sites at adsorbent surface (Hai et al. 2015) and saturation happens when the dye molecule fill the site where no more adsorption can occur at that site (Langmuir 1918). The linear equation of Langmuir isotherm equation is given by Eq. 3:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \times K_L} + \frac{1}{Q_0} \times C_e \qquad (3)$$

Where, C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate that adsorbed per unit mass of adsorbent (mg/g), Q_0 is the maximum monolayer adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant related to the free energy of adsorption (L/mg). The constant values are evaluated from intercept and slope of the linear plot of experimental data of (C_e/q_e) versus C_e. The basic characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor. The Freundlich model is the most widely met isotherm. The first model is empirical and is based on the following relation between the adsorbed quantity q and remained solute concentration C is as Eq. 4:

$$q_e = F \times C_e^{\,n} \qquad (4)$$

Where, F (L/kg) and n (dimensionless) being two Freundlich constants (n < 1). The Temkin adsorption isotherm interaction and the material adsorb to be examined by a specified factor (Shah et al. 2015). The Temkin isotherm model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly due to adsorbent-adsorbate interactions. The Temkin model is expressed as Eq. 5 (Ijagbemi et al. 2009):

$$q_e = B \ln(A) + B \ln(C_e) \qquad (5)$$

Where B and A are the Temkin constants and can be determined by a plot of q_e versus $\ln(C_e)$. The D–RK isotherm can be expressed by Eq. 6-a and b:

$$q_e = q_s\, e^{(-K_{DR} \times \varepsilon^2)} \qquad \text{(6-a)}$$

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad \text{(6-b)}$$

Where, T and R are the temperature (°K) and gas constant (j mol^{-1} K^{-1}), respectively. Also, q_s (mg/g) is a constant in the Dubinin-Radushkevich isotherm model which are related to adsorption capacity, K_{DR} (mol^2/kJ^2) is a constant in related to the mean free energy of adsorption.

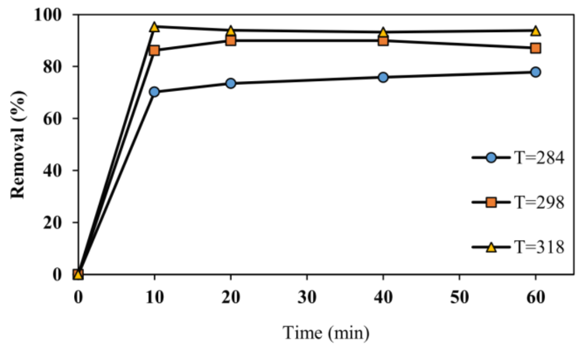

Fig 8. The effect of temperature (˚K) in the removal of MG dye at pH=9, C0=10 ppm.

Sips isotherm model can be expressed by Eq. 7:

$$q_e = q_{max} \times \left(\frac{k_s\, C_e\, e^{n_s}}{1 + k_s\, C_e\, e^{n_s}}\right) \qquad (7)$$

Where, k_s constant Sips isotherm and q_{max} maximum absorption capacity. R–P isotherm can be expressed by Eq. 8:

$$q_e = \left(\frac{q'_{mon}\, b_{RP}\, C_e}{1 + b_{RP}\; C_e^{\,\alpha}}\right) \qquad (8)$$

Where, q'_{mon} and b_{RP} are parameters of the R–P isotherm model. Isotherm parameters for the adsorption of dye onto high porous SMW adsorbent at 284 °K are shown in Table 3. According Table 3, it was found that the Sips isotherm for MG dye removal showed better correlation with the experimental data than other isotherms. So, adsorption isotherms constants (R^2) showed that the uptake of dye onto high porous SMW adsorbent could be described by the Sips model for MG dye.

Table 3. Langmuir, Freundlich, Temkin, Sips, D–RK and R–P isotherm constants for the adsorption of MG dye on high porous SMW adsorbent.

Isotherm Model	Coefficient	Value	Isotherm Model	Coefficient	Value
Langmuir	q_m	0.598	Freundlich	K_F	1.819
	K_L	0.566		1/n	0.101
	R^2	0.732		R^2	0.612
D–RK	X_m	444.167	Sips	$q_{maxsips}$	3.08
	K	4.00E-06		K_{sips}	– 360.75
	E	3.54E+02		n_{sips}	– 5.50
	R^2	0.593		R^2	0.946
Temkin	B	183.910	R –P	B_{RP}	– 4.29E-05
	K_t	1.845		q'_{mon}	– 41295.01
	R^2	0.291		α	– 9.422
				R^2	0.907

4.2. Adsorption kinetic

In the present study, the adsorption kinetics of MG dye onto high porous SMW adsorbent were modelled using four common models consist of pseudo-first-order, pseudo-second-order, Elovich and intra – particle diffusion. Four kinetics models are listed in as Eq. 9–12 (Maneechakr and Karnjanakom, 2017):

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \quad (9)$$

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \quad (10)$$

$$\frac{dq_t}{dt} = a_e \exp(-b_e \times q_t) \quad (11)$$

$$q_t = K_i \times t^{0.5} \quad (12)$$

Where, in Eq. 9, K_1 (min^{-1}) is the rate constant of the pseudo first order adsorption kinetic. In Eq. 10, K_2 (g/mg min) is the adsorption rate constant of pseudo second order kinetic model. In Eq. 11, a_e initial adsorption rate (mg/g min) and b_e (g/mg) are the parameters of the Elovich rate equation obtained from the linear regression analysis of the q_t versus ln (t). Also, in Eq. 12, K_i (mg $g^{-1}min^{-1/2}$), is the rate constants of intra-particle diffusion. The values of parameters obtained by different kinetic models for the adsorption of dye onto high porous SMW adsorbent are shown in Table 4.

Based on Table 4, the correlation coefficients for the pseudo-second order kinetic model for MG dye is 0.9995. So, adsorption kinetic constants (R^2) showed that the uptake of dye onto high porous SMW adsorbent could be described by the pseudo–second order kinetic model for MG dye.

Table 4. The values of parameters obtained from different kinetic models for the adsorption of MG dye onto high porous SMW adsorbent.

Kinetic Model	Coefficient	Value
Pseudo first–order	K_1	0.021
	q_e	179.9
	R^2	0.961
Pseudo second–order	K_2	0.326
	q_e	2.916
	R^2	0.9995
Elovich	b_e	0.025
	a_e	61.180
	R^2	0.934
Intra–particle diffusion model	K_i	0.088
	R^2	0.981

4.3. Adsorption thermodynamic

The adsorption amounts of MG dye onto high porous SMW adsorbent at temperatures of 284, 298 and 318 °K have been studied. Using these temperatures through the Van't Hoff (Eq. 13), thermodynamic parameters can be calculated (López-García et al. 2013).

$$\log(K_d) = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \quad (13)$$

Where, ΔS˚ (KJ/mol K) and ΔH˚ (KJ/mol) are entropy and enthalpy, respectively. R (8.314 J/mol K) is the gas constant, T (°K) is absolute temperature, also, in Eq. 14, K_d is the equilibrium constant and a is the amount of adsorption at equilibrium time that K_d is calculated using Eq. 14:

$$K_d = \frac{a}{1-a} \quad (14)$$

ΔS˚ and ΔH˚ can be calculated using intercept and slope of linear regression of $\log(K_d)$ versus 1/T, respectively. As well as Gibbs free energy is determined from Eq. 15-a and b (Khan and Singh, 1987):

$$\Delta G° = -RT\, ln(K_d) \quad (15\text{-a})$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (15\text{-b})$$

By using equations of Eq. 13-15, the parameters of ΔS˚, ΔH˚ and ΔG˚ have been calculated and are shown in Table 5.

The Negative values of ΔH˚ indicate the exothermic nature of the adsorption of MG dye onto high porous SMW adsorbent in the temperature range of 284–318 °K. Can conclude that positive changes in entropy act to increase the MG dye adsorption and positive changes in enthalpy act to reduce adsorption of dye.

Table 5. Values of thermodynamic parameters for the adsorption of MG dye onto high porous SMW adsorbent.

ΔH˚ (kJ mol^{-1})	ΔS˚ (J mol^{-1}K^{-1})	ΔG˚ (KJ Mol^{-1})			
		284 °K	298 °K	308 °K	318 °K
– 21.21	+ 0.028	– 13.16	– 12.79	– 12.51	– 12.22

4.4. Adsorbent reusing

Reusing high porous SMW adsorbent is an important factor which aims to utilize the adsorbent in wastewater treatment. So, in this paper we collected utilized adsorbent and secondly were washed with NaCl 1 M for 2 h, then the NaCl/adsorbent mixture was filtered. Also, the adsorbent was washed with NH_4OH 1 M for 2 h. Finally after filtration for expelling the NH^+_4 that sits on the OH^- function, adsorbent were washed with deionized water and then heated in 60 °C for 2 h. This work has been done four times for adsorbent after using and the sorption process was considered for MG dye. The results of high porous SMW adsorbent reusing for MG dye sorption are shown in Figure 9. According to Figure 9, the sorption of MG dye by reactivating high porous silicate mining waste adsorbent for four times kind of decreased that is due to reduction of the adsorbents specific surface area because of coagulation and agglomeration of adsorbent particles and the lack of quite clean adsorbent that was collected and reactivated from previous steps.

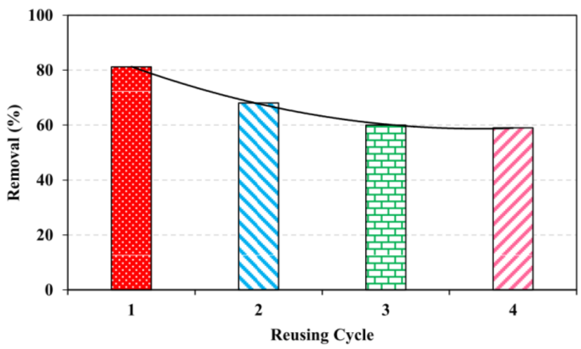

Fig 9. Results of high porous SMW adsorbent reusing for MG dye sorption.

5. Conclusions

High porous SMW adsorbent which is prepared from Syah Kamar Polymetal Porphyry mine waste, can be a very effective adsorbent for removal of malachite green dye from aqueous solution. The chemical structure and physical properties of SMW adsorbent have been studied using XRD, XRF, SEM and FT-IR analysis. The effect of parameters of pH, adsorbent dosage, initial concentration, contact time and temperature on adsorption process has been studied. The optimum pH for adsorption of malachite green dye is 9. With increasing of the amount of SMW adsorbent, adsorption followed an increasing trend and with increasing of concentration, the percentage of malachite green dye adsorption has been decreased. Rising temperature results in rising of malachite green dye adsorption. The equilibrium and kinetic of adsorption process have been investigated. According to the comparison between experimental data and models, it has been proven that Sip isotherm and pseudo-second order kinetic models have the most agreement. Also, based on thermodynamic study and negative value of Gibbs energy (ΔG˚) show that the sorption of dye onto high porous SMW adsorbent was spontaneous process. The negative amount of ΔH˚ suggests that the reaction of sorption of malachite green dye onto SMW adsorbent is an exothermic reaction. The value of ΔS˚ is slightly and it means that entropy is not influential parameter. Also, the positive low values of ΔS˚ indicate low randomness at the solid/solution interface during the uptake of malachite green dye onto high porous SMW adsorbents. The negative value of ΔH˚ and positive value of ΔS˚ imply that enthalpy and entropy have favorable effect.

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References:

Bailey RA, Clark HM, Ferris JP, Krause S, Strong RL, Bailey RA, Clark HM, Ferris JP, Krause S, Strong RL (2002) Water systems and water treatment, *Chemistry of the Environment* 415–442.

Dang TD, Banerjee AN, Tran QT, Roy S (2016) Fast degradation of dyes in water using manganese-oxide-coated diatomite for environmental remediation, *Journal of Physics and Chemistry of Solids* 98: 50–58.

Hai Y, Li X, Wu H, Zhao S, Deligeer W, Asuha S (2015) Modification of acid-activated kaolinite with TiO_2 and its use for the removal of azo dyes, *Applied Clay Science* 114: 558–567.

Han H, Wei W, Jiang Z, Lu J, Zhu J, Xie J (2016) Removal of cationic dyes from aqueous solution by adsorption onto hydrophobic/hydrophilic silica aerogel, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 509: 539–549.

Hosseini F, Sadighian S, Hosseini-Monfared H, Mahmoodi N.M (2016) Dye removal and kinetics of adsorption by magnetic chitosan nanoparticles, *Desalination and Water Treatment* 57(1): 1–9.

Ijagbemi CO, Baek MH, Kim DS (2009) Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, *Journal of Hazardous Materials* 166(1): 538–46

Khan AA, Singh RP (1987) Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H^+, Na^+ and Ca^{2+} forms, *Colloids and Surfaces* 24(1): 33–42.

Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal of the American Chemical Society* 40(9): 1361–1403.

Li X, Zhang Y, Jing L, He X (2016) Novel N-doped CNTs stabilized Cu_2O nanoparticles as adsorbent for enhancing removal of Malachite Green and tetrabromobisphenol A, *Chemical Engineering Journal* 292: 326 –339.

López-García M, Lodeiro P, Herrero R, Barriada JL, Rey-Castro C, David C, De Vicente MES (2013) Experimental evidences for a new model in the description of the adsorption-coupled reduction of Cr(VI) by protonated banana skin, *Bioresource Technology* 139: 181–189.

Mahmoodi NM, Abdi J, Afshar-Bakeshloo Z, Abdi J, (2016a) Synthesis and characterization of the functionalized nanoparticle and dye removal modeling, *Desalination and Water Treatment* 57(50) 1–12.

Mahmoodi NM, Hosseinabadi-Farahani Z, Bagherpour F, Khoshrou MR, Chamani H, Forouzeshfar F (2016b) Synthesis of CuO–NiO nanocomposite and dye adsorption modeling using artificial neural network, *Desalination and Water Treatment* 57: 17220–17229.

Mahmoodi NM, Hosseinabadi-Farahani Z, Chamani H (2016c) Synthesis of nanostructured adsorbent and dye adsorption modeling by an intelligent model for multicomponent systems, *Korean Journal of Chemical Engineering* 33: 902–913.

Mahmoodi NM, Hosseinabadi-Farahani Z, Chamani H (2015) Nanostructured adsorbent (MnO_2): Synthesis and least square support vector machine modeling of dye removal, *Desalination and Water Treatment* 57: 21524–21533.

Maneechakr P, Karnjanakom S (2017) Adsorption behaviour of Fe(II) and Cr(VI) on activated carbon: Surface chemistry, isotherm, kinetic and thermodynamic studies, *The Journal of Chemical Thermodynamics* 106: 104–12.

Moussavi G, Mahmoudi M (2009) Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles, *Journal of Hazardous Materials* 168(2): 806–812.

Polak J, Jarosz-Wilkolazka A, Szuster-Ciesielska A, Wlizlo K, Kopycinska M, Sojka-Ledakowicz J, Lichawska-Olczyk J, (2016) Toxicity and dyeing properties of dyes obtained through laccase-mediated synthesis, *Journal of Cleaner Production* 112: 4265–4272.

Rehman MSU, Kim I, Han JI (2012) Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass, *Carbohydrate Polymers* 90(3): 1314–1322.

Senthamarai C, Kumar PS, Priyadharshini M, Vijayalakshmi P, Kumar VV, Baskaralingam P, Thiruvengadaravi KV, Sivanesan S (2013) Adsorption behavior of methylene blue dye onto surface modified Strychnos potatorum seeds, *Environmental Progress & Sustainable Energy* 32(3): 624–632.

Seifpanahi-Shabani KS, Doulati-Ardejani F, Badii Kh, Olya M.E (2013) Preparation and characterization of novel nano-mineral for the removal of several heavy metals from aqueous solution: Batch and continuous systems, *Arabian Journal of Chemistry* article in press.

Shah J, Jan MR, Ul-Haq A, Zeeshan M (2015) Equilibrium, kinetic and thermodynamic studies for sorption of Ni(II) from aqueous solution using formaldehyde treated waste tea leaves, *Journal of Saudi Chemical Society* 19(3): 301–310.

Talarposhti AM, Donnelly T, Anderson GK (2001) Colour removal from a simulated dye wastewater using a two-phase anaerobic packed bed reactor, *Water Research* 35(2): 425–432.

Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review, *Advances in Colloid and Interface Science* 209: 172–184.

Zhang F, Ma B, Jiang X, Ji Y (2016) Dual function magnetic hydroxyapatite nanopowder for removal of malachite green and Congo red from aqueous solution, *Powder Technology* 302: 207–214.