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USING WASTE FOUNDRY SAND FOR THE REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTIONS - KINETIC AND EQUILIBRIUM STUDIES

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Abstract

The aim of this study was to examine the adsorption of malachite green dye from aqueous solutions on the waste foundry sand. The effects of contact time, adsorbent amount, pH and initial dye concentration were investigated. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin adsorption isotherm models. The adsorption capacity of waste foundry sand for the removal of malachite green dye was determined with the Langmuir and found to be 23.29 mg/g. The adsorption isotherm constants were employed to calculate thermodynamic parameters like Gibbs free energy, changes in enthalpy and entropy. The adsorption kinetic data were modeled using the pseudo-second order, intraparticle diffusion and Elovich isotherm model. Adsorption data of the malachite green dye was fitted well by the pseudo-second-order model. In the present study, several error analysis methods were used in order to confirm the best fitting kinetic system, namely the coefficient of determination (R^2) and the sum of error squared (SSE). We used a statistical approach for comparing models, namely Akaike's information criterion (AIC), which has had a fundamental impact in statistical model evaluation problems.

Keywords: adsorption, isotherm, malachite green, waste foundry sand

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1. Introduction

Dyes are used in large quantities in many industries that include textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals and food. Textile industry discharges high dirtiness, wastewater amount, and dyestuff dissolved. Because textile industry consists of very different processes, textile wastewater can be diminished in terms of polluting loads by applying physical, biological and chemical treatment methods. One of the methods used for the removal of colour from wastewater of textile industry is adsorption. Activated carbon is one of the most used adsorbents because of high adsorption efficiency. Despite the fact that the adsorption capacity of active carbon is high, its high cost determined the development of new research to find cheaper adsorbents. Recently, using more economical

substances in adsorption of dyestuff becomes common. Several materials have been evaluated as adsorbent like volatile ash, natural clay, polyurethane foams, apricot seed, walnut cover, sepiolite and zeolite (Amani-Ghadima et al., 2013; Apostol et al., 2016; Auta and Hameed, 2015; Ay et al., 2009; Bingol et al., 2010; Dikmen et al., 2015; Duman et al., 2015; Garg et al., 2004; Khambhaty et al., 2016; Neta et al., 2011; Önal et al., 2005).

Foundry sand is high quality silica sand with uniform physical characteristics. Classification of foundry sands depends upon the type of binder systems. Generally, two types of binder systems are used and based on that, foundry sands are classified as: clay bonded systems (green sand) and chemically bonded systems. Green sand molds are used to produce about 90% of casting volume. Green sand is composed of high quality silica sand (85–95%),

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bentonite clay (4–10%) as a binder, a carbonaceous additive (2–10%) to improve the casting surface finish, and water (2–5%). Green sand is the most commonly used recycled foundry sand for beneficial reuse. It is black in color due to carbon content, having a clay content that results in percentage of material that passes a 200 sieve and adheres together due to clay and water. Chemically bonded sands are used both in core making where high strengths are necessary to withstand the heat of molten metal, and in mold making. Most chemical binder systems consist of an organic binder that is activated by a catalyst, although some systems use inorganic binders. Chemically bonded sands are generally lighter in color and in texture than clay bonded sands (Bhimani et al., 2013; Danko, 2010; Danko, 2011; Siddique et al., 2009).

In United States alone, this foundry Industry estimates that approximately 100 million tons of sand is used in production annually, of that 6–10 million tons are discarded annually and are available to be recycled into other products or are used in other industries. The automotive industries and its parts are the major generators of foundry sand. Foundries purchase high quality size-specific silica sands for use in their molding and casting operations (Danko, 2013, Siddique, 2008; Siddique et al., 2009).

Metal casting foundries in the US disposed approximately 9 million metric tons of waste foundry sand in landfills in 2000. Given the national average landfill tipping fee of foundry by products of US \$15–75 per ton inclusive of storage, transportation and labor costs, the annual cost of waste foundry sand disposal was around US\$ 135–675 million. The considerable disposal expense has made the current practice of waste foundry sand disposal in landfills less favorable. Besides the financial burden to the foundries, landfilling waste foundry sand also makes them liable for future environmental costs, remediation problems, and regulation restrictions. This issue is increasingly addressed by alternate scenarios of beneficially reusing waste foundry sand. Significant efforts have been made in recent years to use foundry sand in civil engineering construction (Lin et al., 2012; Siddique et al., 2010; Yucel et al., 2006). Some of the application areas included highway bases and retaining structures, landfill liners, asphalt concrete, hydraulic barrier, flowable fill, pavement bases, rehabilitation and wastewater treatment works. There are only few studies about how waste foundry sand have been used to remove heavy metals such as chromium (VI), copper, nickel and zinc ions from aqueous solutions, and has not been previously used as an adsorbent for the removal of textile dyes from aqueous solutions (Campos et al., 2013; Faisal and Ahmed, 2015; Lee et al., 2004; Malina et al., 2012; Shankara et al., 2012; Strkalj et al., 2013).

The objective of this study was to investigate the removal of malachite green dye by waste foundry sand by adsorption. The effects of contact time, adsorbent amount, pH, initial dye concentration and

adsorption temperature were investigated. Experimental data have been analyzed by adsorption isotherms, kinetics parameters. In addition, the equilibrium thermodynamic parameters are determined for the malachite green on waste foundry sand.

2. Experimental

2.1. Materials

The waste foundry sand generated from foundries and arising in high amounts in casting process are currently disposed in landfills. It is known that the recovery and reuse of wastes instead of disposal will provide important savings both in production costs and treatment and disposal costs via minimization of waste amounts. The increase in the ratio of production input of recovered wastes leads to a reduction in the pressure of economical activities on natural resources, and also in the pressure of wastes on the environment.

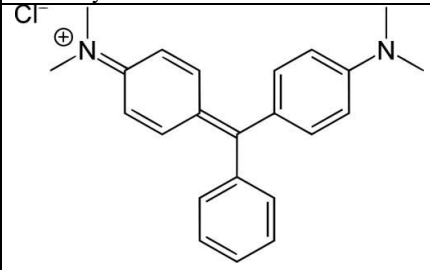
The waste foundry sand used in the experimental study was obtained locally in Samsun, Turkey. This sand is used as foundry sand in steel and metal molding facilities for the production of metal-steel parts at high temperatures. The chemical composition of the waste foundry sand was determined by using an X-ray fluorescence spectrometer (Thermo ARL). The chemical of foundry sand is given Table 1. As seen in the Table 1, the waste foundry sand contained significant levels of SiO₂ (79.60%), Al₂O₃ (5.30%) and Fe₂O₃ (3.108%). The BET surface area of the waste foundry sand was determined from N₂ adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Nova 2200e). The BET surface area of waste foundry sand which was primarily contributed by micropores was determined 7.218 m²/g.

The basic dye, malachite green (C₂₃H₂₆ClN₂), was selected for adsorption studies. The stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of malachite green in 1000 ml distilled water. Table 2 shows some properties of malachite green dye. The initial pH of solutions was adjusted to the required value by using NaOH or HCl solutions.

Table 1. Chemical composition of waste foundry sand sample (wt %)

<i>Major components</i>	<i>(wt %)</i>
Al ₂ O ₃	5.30
CaO	1.40
Fe ₂ O ₃	3.10
K ₂ O	0.60
MgO	2.30
MnO	0.20
Na ₂ O	0.60
P ₂ O ₅	0.10
SiO ₂	79.60
TiO ₂	0.40
<i>others</i>	5.90

Table 2. Some properties of malachite green dye

Basic dyes properties	Malachite green
C.I. No	42000
CAS No	5596-64-2
Chemical Formula	C ₂₃ H ₂₆ ClN ₂
Molecular Weight	364.92
Melting Point	164 OC
C.I. Name	Basic Dye
Molecular Structure	

All experiments were conducted in duplicate and the average values were used for data analysis.

2.2. Method

Waste foundry sand, black in color, 35-mesh size, was used as an adsorbent. It was dried, and then washed with distilled water several times to remove any dust and other water-soluble impurities. The washed sample was dried at 105 °C in an oven before use in the adsorption studies. Adsorption properties of waste foundry sands were evaluated by depending on different adsorption conditions such as different initial dye concentrations, contact times, adsorbent dosage, pH, and temperature. The concentrations of the dyes were determined using UV/Vis Spectrophotometer.

The removal efficiency (E) of the waste foundry sand on malachite green dye was calculated according to Eq. (1):

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of the dye solution and C is the final concentration of the dye solution.

2.3. Adsorption studies

In order to determine the effect of contact time, initial dye concentration, adsorbent dosage and pH on malachite green dye removal efficiency, batch experiments were conducted. A stock solution 1000 mg/L of dye was prepared in distilled water and was diluted according to the working concentration. Dye concentration was measured using a UV-Vis Spectrophotometer at λ_{max} of 620 nm. The dye solution (100mL) at desired concentration (25 and 400 mg/L), pH (3 and 9), adsorbent dosage (5 and 40

g/L), contact time (5 and 240 min) and adsorption temperature (20°C and 70°C) taken in 250 mL Erlenmeyer flasks was used. The flasks were kept under agitation in a rotating shaker at 150 rpm for 2h.

3. Results and discussion

3.1. Material characterization

The crystalline phase composition of the waste foundry sand used in this work was characterized by SEM (FEI Quanta 400 MK2) in Fig. 1. The waste foundry sand is taken in the wavelength range of 400-4000 cm⁻¹. FTIR (Perkin-Elmer Spectrum Two) spectrum was given in Fig. 1a. As a result of FTIR analysis, the organics of foundry sand were identified as a mixture of the aliphatic hydrocarbon type.

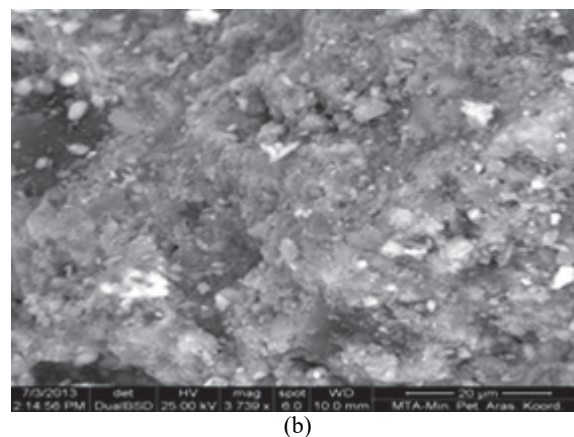
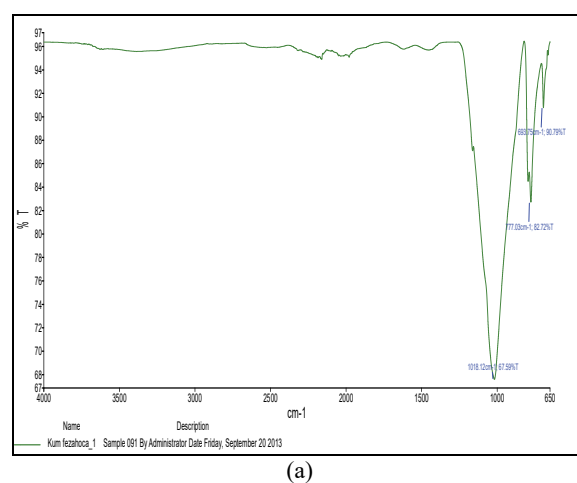


Fig. 1. FTIR Spectrum and SEM analyses of waste foundry sand

3.2. Effect of contact time on the removal of malachite green

The effects of contact time in the range 5-240 min were studied using a constant concentration of malachite green dye solution at 23°C. The removal percentage of the malachite green as a function of contact time is shown in Fig. 2. The results showed that the removal of malachite green increases with

time rapidly and saturation in about 120 min. The results clearly show that if contact time for waste foundry sand is increased from 5 to 120 minutes, the removal efficiencies increase from 80.40% to 95.80%. The rate of percent malachite green removal is higher in the beginning due to a larger surface area of the waste foundry sand being available for the adsorption of the malachite green.

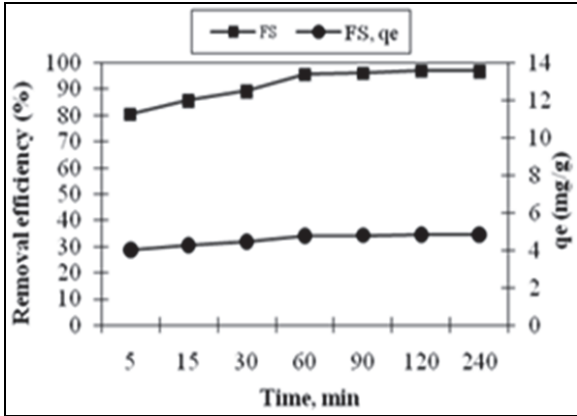


Fig. 2. Effect of contact time on malachite green adsorption (T: 20°C, Co: 50 mg/L, dosage: 5 g/L)

3.3. Effect of waste foundry sand amount on the removal efficiency

Fig. 3 shows the effect of the amount of waste foundry sand dosage on the malachite green removal. As the waste foundry sand amounts increased, the removal efficiencies increased. The removal efficiencies for 5 g/L of waste foundry sand was found to be 92.2%, but as the waste foundry sand amounts were increased to 40 g/L, removal efficiency was found to be 98.4%. These results show that removal efficiency was increased with increasing amount of the waste foundry sand.

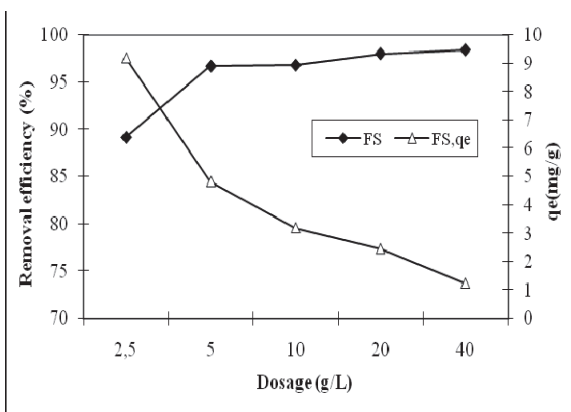


Fig. 3. Effect of waste foundry sand amount on malachite green adsorption (T: 20°C, Co: 50 mg/L, time: 2h)

3.4. Effect of initial dye concentration

The effect of initial malachite green concentration in the range of 25-400 mg/L on the adsorption was investigated under the specified

conditions. Fig. 4 shows the adsorption of malachite green on waste foundry sand as an initial dye concentration.

The percent adsorption of malachite green is inversely related to the initial dye concentrations. Percentage of malachite green removal decreased as its concentration increased at fixed adsorbent dosage. As can be seen from Fig. 4, increasing the dye concentration led to an increase in the dye adsorption by waste foundry sand. This can be attributed to the effective pore diffusivity decrease with increasing initial dye concentration. Increasing the dye concentration led to an increase in the malachite green adsorption by waste foundry sand. The maximum adsorption capacity of waste foundry sand was found to be 22.5 mg/g for 400 mg/L dye concentration. Waste foundry sand in this study, are a mixture of sand, bentonite, and coal dust. The coal dust and bentonite provide sorption sites for heavy metal and dye ions (Lee et al., 2004).

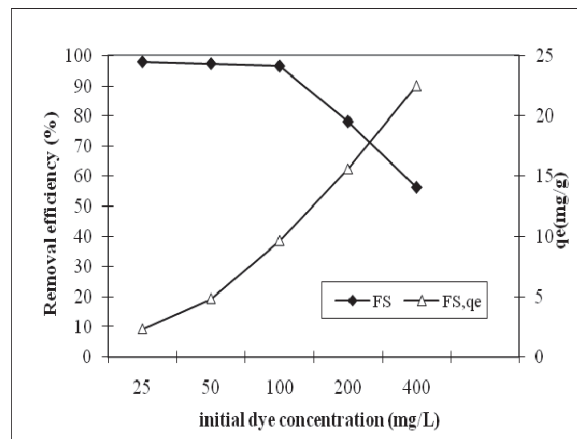


Fig. 4. Effect of initial concentration on malachite green adsorption (T: 20°C, dosage: 10 g/L, time: 2h)

3.5. Effect of pH on the removal of malachite green dye

The pH of the aqueous solutions is an important variable and controls the adsorption between the adsorbent and aqueous interface. The adsorption extent of dyes is strongly affected by the pH of solution (Fernandes et al., 2007; Wang et al., 2005). The effect of pH on removal of the malachite green was studied by keeping the dosage of waste foundry sand, concentration of solution, and contact time constant and varying the pH of the medium from 3 to 9 Fig. 5 represents the effect of pH on the dye adsorption by waste foundry sand. Adsorption of the malachite green increased with an increase in pH. The increase of malachite green adsorption on waste foundry sand with increasing pH values can be explained by the electrostatic interaction between cationic dyes and negatively charged waste foundry sand surface. At low solution pH, the amount of dye sorbed was found to be low. At pH 3, the removal efficiency of dye by waste foundry sand was 77.40%. The optimum pH for the adsorption of the malachite

green was found to be in the range 6-8. At pH 7, the removal efficiency of dye by waste foundry sand was obtained 97.68%.

Malachite green is a basic dye. In water, it produces cation (C+) and reduces ions (CH+). The basic dye will become protonated in the acidic medium and the positive charge density would be located more and the dye molecules at low pH, resulting the lower adsorption (Baek et al., 2010; Bukallah et al., 2007).

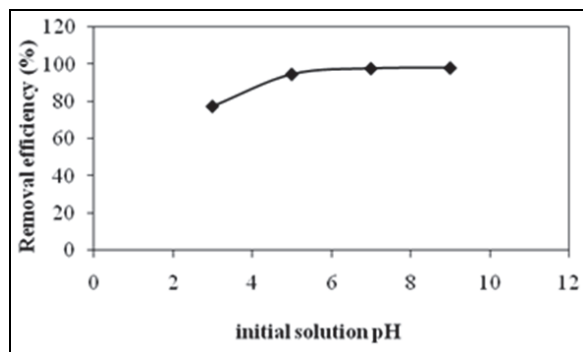


Fig. 5. Effect of pH on malachite green adsorption on waste foundry sand (T: 20°C, Co: 50 mg/L, dosage: 5 g/L, time: 2h)

3.6. Effect of temperature on the removal of malachite green dye

The effect of temperature on the removal of malachite green was studied in the range of 20-70°C (Fig. 5). The results are presented in Fig. 6. For a contact time of 60 min, malachite green adsorption efficiencies for waste foundry sand was found to be 95.45% – 99.20% at 20 - 70°C, respectively.

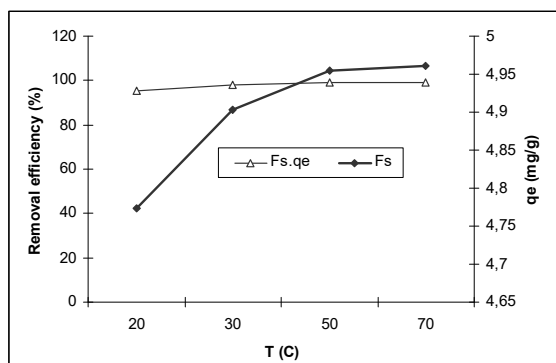


Fig. 6. Effect of temperature on the removal of malachite green dye (Co: 50 mg/L, dosage: 5 g/L, time: 2h)

3.7. Adsorption isotherms models

The equilibrium adsorption isotherms are among the most important data to understanding the mechanism of the adsorption systems. Adsorption isotherms give an idea about the adsorption capacity of an adsorbent for the removal of some compounds. The sorption data have been subjected to different sorption isotherms. In this research, to determine the mechanism of malachite green adsorption on waste

foundry sand, the experimental data were applied to the Langmuir, Freundlich, and Temkin isotherm equations. The data conform to the linear form of Langmuir model (Eq. 2), where, q_e is the amount adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), and q_m and K_L are the Langmuir constants related to the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively.

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

Linear plots of C_e/q_e vs. C_e were employed to determine the value of q_m and K_L . The data for the sorption of metal ion by the clays has been processed in accordance with a linear form of the Langmuir isotherm equation. The linear model, which describes the accumulation of solute by the sorbent was shown to be directly proportional to the solution concentration.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L , which is defined as given by Eq. (3):

$$R_L = 1/(1 + K_L C_o) \quad (3)$$

where C_o is the initial concentration and K_L is the Langmuir isotherm constant. The feasibility criteria of the process can be judged as unfavorable ($R_L > 1$), irreversible ($R_L = 0$), favorable ($0 < R_L < 1$) or linear ($R_L = 1$) patterns. The R_L values varied within a range of, 0.016 - 0.027 for waste foundry sand, respectively, for the initial malachite green concentration values of 25-400mg/L. They are in the range of 0 - 1, which indicates favorable adsorption.

The effect of concentration on sorption was applied to different isotherm models to find a suitable model to instruct the further experimental design. Several isotherm equations are available. In this research, in order to determine the mechanism of malachite green adsorption on the waste foundry sand the experimental data was applied to the Freundlich and Temkin isotherm equations (Ahmad and Alrozi, 2011; Bulut et al., 2008).

The Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface; it is given in (Eq. 4):

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

where q_e the amount of dye ions adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration in mg/L, K is roughly an indicator of the adsorption capacity (mg/g), n is a characteristic constant for the adsorption system (1/g).

The n values between 1 and 10 (i.e., $1/n$ less than 1) indicate the beneficial adsorption. A relatively $n \ll 1$ indicates that adsorption intensity is

favorable over the entire range of concentrations studied, while $n > 1$ means that adsorption intensity is favorable at high concentrations but much less at lower concentrations (Banu and Güçlü, 2009; Zhao et al., 2008). For the adsorption of malachite green on waste foundry sand, the n values were above beneficial adsorption.

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin, 1940). The Temkin isotherm is represented by Eq. (5):

$$q_e = \frac{RT}{b} \ln K_T C_e \tag{5}$$

Eq. (5) can be expressed in its linear form as Eq. (6):

$$q_e = B \ln K_T + B \ln C_e \tag{6}$$

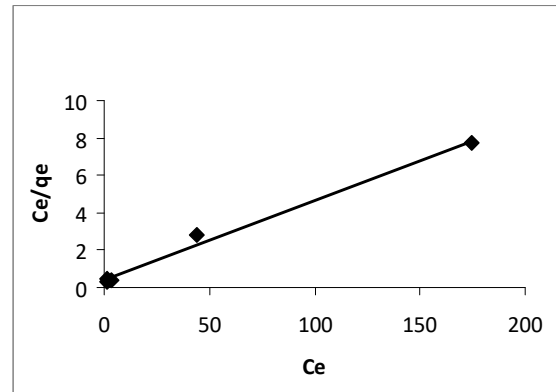
where T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol K), K_T is the equilibrium binding constant (L/mg), and b is the variation of adsorption energy (kJ/mol). B is the Temkin constant related to the heat of adsorption (kJ/mol). The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbate. The Temkin isotherm plot is presented in Fig. 7c and the isotherm parameters are given in Table 3.

Table 3. Isotherm parameters for the malachite green adsorption on waste foundry sand

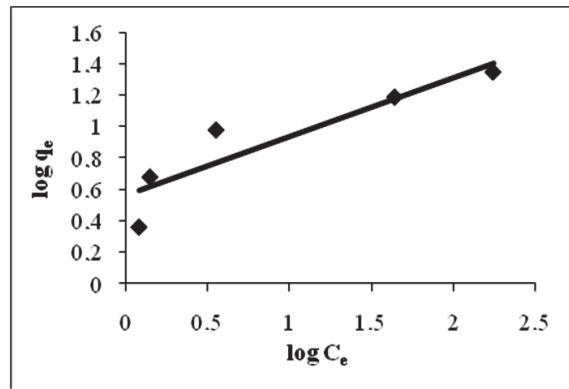
Isotherms	Waste Foundry Sand
Langmuir constants	
K_L (mg/g)	23.290
a_L (g/L)	0.098
R^2	0.991
Freundlich constants	
K_F (mg/g)	3.717
$1/n$ (g/L)	2.673
R^2	0.839
Temkin constants	
A (L/g)	2.387
B (J/mol)	3.644
R^2	0.971

The Temkin adsorption potential, K_T of waste foundry sand for MG is 2.3879. The Temkin constant, b , related to heat of sorption was 0.621 kJ/mol. It has been reported (Ho et al., 1996) that the typical range of bonding energy for ion-exchange mechanism is 8-16 kJ/mol. The low values in this study indicates a weak interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study. The parameters for the Langmuir, Freundlich and Temkin isotherms

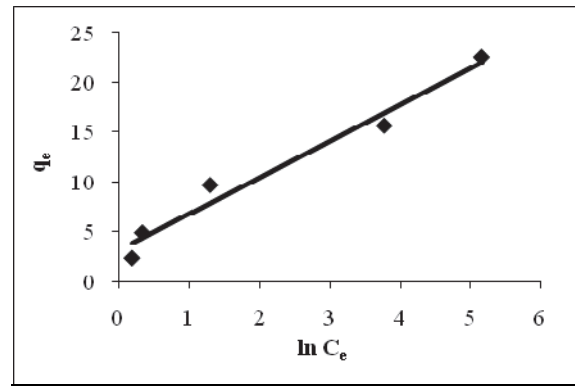
obtained from experimental data and the related correlation coefficients are given in Table 3. The data obtained were well fitted with the Langmuir models (Fig. 7).



(a)



(b)



(c)

Fig. 7. (a) The Linearized Langmuir isotherm of malachite green uptake by waste foundry sand; (b) The Linearized Freundlich isotherm of malachite green uptake by waste foundry sand; (c) The Linearized Temkin isotherm of malachite green uptake by waste foundry sand.

Comparison of adsorption isotherms

It is customary in batch adsorption studies to fit the equilibrium uptake data to several isotherms, then to use R^2 to compare the goodness of fit and select the best isotherm model. With the best isotherm supposedly identified, conclusions are usually presented regarding the homogeneity of the adsorbent surface and the mechanism of adsorption.

Akaike's Information Criterion (*AIC*) is a well established statistical method that can be used to compare models. It is based on information theory and maximum likelihood theory, and as such, it determines which model is more likely to be correct and quantifies how much more likely. For a small sample size, *AIC* is calculated for each model from (Eq. 7):

$$AIC = N \ln \left(\frac{SSE}{N} \right) + 2N_p + \frac{2N_p(N_p + 1)}{N - N_p - 1} \quad (7)$$

where *N* is the number of data points, *N_p* is the number of parameters in the model and *SSE* is sum of the error squares.

The adsorption isotherms models having two parameters can be transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. But, the models having more than two adjustable parameters are not fitted to experimental data by linear regression or graphical means. In this case it is necessary to apply nonlinear least squares analysis. For that reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared (*SSE*) between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel. The term *SSE* generally refers to a "sum of squared errors". The errors are the difference between the observed value and the value predicted by the model (Eq. 8).

$$SSE = \sqrt{\sum (q_{exp} - q_{cal})^2 / N} \quad (8)$$

where the subscripts "exp" and "cal" are the experimental and calculated values of *q*, respectively and *N* is the number of measurements.

The results of nonlinear regression are presented in Table 4. This study concluded, on the basis of *R*² comparison to waste foundry sand, that the Langmuir isotherm is the best fit. Accordingly, *AIC* values to waste foundry sand were calculated for Langmuir (14.83), Freundlich (14.02) and Temkin (14.10) isotherms, respectively. Having a smaller *AIC* value to waste foundry sand suggests that Freundlich isotherms are more likely to be the best fit.

Table 4. Nonlinear regression for isotherm parameters

<i>Isotherms</i>	<i>Waste Foundry Sand</i>
Langmuir	
SSE	13.157
AIC	14.837
Freundlich	
SSE	11.156
AIC	14.021
Temkin	
SSE	11.372
AIC	14.108

The parameters of each isotherm equation can be determined by minimizing the *SSE*. The best-fit model should have the least *SSE* value; therefore, this model can be obtained by comparing the *SSE* of each model. The *SSE* values are compared in Table 3. By comparing the *SSE* of different models in the three isotherm systems, it seems that Freundlich isotherm was the best fit although the *SSE* for the Langmuir and the Temkin are very similar. Comparison of adsorption capacity (*q_m*) for the adsorption of MG by different adsorbents is presented in Table 5. The *q_m* for the adsorption of MG is lower than that for general adsorbents used for MG.

Table 5. Comparison of adsorption capacities of various adsorbents for MG

<i>Type of adsorbent</i>	<i>q_m (mg g⁻¹)</i>	<i>References</i>
Bentonite	178.60	Bulut et al., 2008
Activated carbon (waste apricot)	116.30	Basar, 2006, Baek et al., 2010
Degreased coffee bean	55.34	
Palm flower based activated carbon	20.46	Nethajia et al., 2010
Aminopropyl functionalized magnesium phyllosilicate	130.64	Lee et al., 2011
Nem sawdust	4.34	Khatti and Singh, 2009
Waste foundry sand	23.29	This study

3.8. Adsorption kinetics

The rate constants of chemical adsorption and intraparticle diffusion for the malachite green adsorption on waste foundry sand were determined using the equations of pseudo-second-order and intraparticle diffusion mode (Ahmad and Alrozi, 2011). Pseudo-second-order kinetics may be expressed as given by Eq. (9):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where *k₂* is the rate constant of adsorption, *q_e* and *q_t* are the amount adsorbed at equilibrium (mg/g).

Integrating this for the boundary conditions *t* = 0 to *t* = *t* and *q_t* = 0 to *q_t* = *q_t* gives (Eq. 10):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (10)$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (7) can be rearranged to obtain Eq. (11):

$$q_t = \frac{t}{(1/k_2 q_e^2) + (t/q_e)} \quad (11)$$

which has a linear form given by Eq. (12):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{12}$$

where k_2 was the rate constant of second-order malachite green adsorption.

Fig. 8a shows the linear plots of t/q_t versus t . The correlation coefficients for the second-order kinetic model were higher than 0.999 indicating the applicability of this kinetic model of the adsorption process of malachite green on waste foundry sand. The calculated q_e values were close to that of experimentally obtained q_e . Thus the adsorption of malachite green on waste foundry sand was explained by the pseudo-second-order kinetic model.

The rate parameter for intraparticle diffusion equation is given using the following (Eq. 13) (Karagöz et al., 2008):

$$q_t = k_{id} t^{1/2} + C \tag{13}$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$).

The plot q versus $t^{1/2}$ is given by multiple linear regions representing the external mass transfer followed by interparticle or pore diffusion. In this model, due to the porous nature of the adsorbent, pore diffusion is expanded to be surface adsorption.

Fig. 8b exhibits the intraparticle diffusion model of malachite green dye adsorption on waste foundry sand. The intra-particle diffusion rate constants k_{id} and correlation coefficients are presented in Table 6. The Elovich equation has general application to chemisorption kinetics. This equation has been applied satisfactorily to some chemisorption data and has been found to cover a large range of slow adsorption.

The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. The rate parameter for the Elovich equation is determined as (Eq. 14) (Cheung et al., 2000; Sprynskyy et al., 2005).

$$q_t = \beta \ln(\alpha) + \beta \ln t \tag{14}$$

where α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are the equilibrium rate constants for Elovich model. The equation constants can be obtained from the slope and intercept of a straight-line plot of q_t against $\ln t$.

The values of constants can be obtained from the slope and intercept of the plots (Fig. 8c). The values of kinetic constants are presented in Table 6. The correlation coefficient for the Elovich model is 0.926.

Comparison of adsorption kinetics

The rate constants and other parameters of the three different batch kinetic equations were obtained by minimizing *SSE* and *AIC* by using the Excel program by iteration. The results of nonlinear regression are presented in Table 7. These results clearly showed that the Pseudo second-order kinetics

model provided the data better than Intraparticle diffusion and Elovich kinetic models.

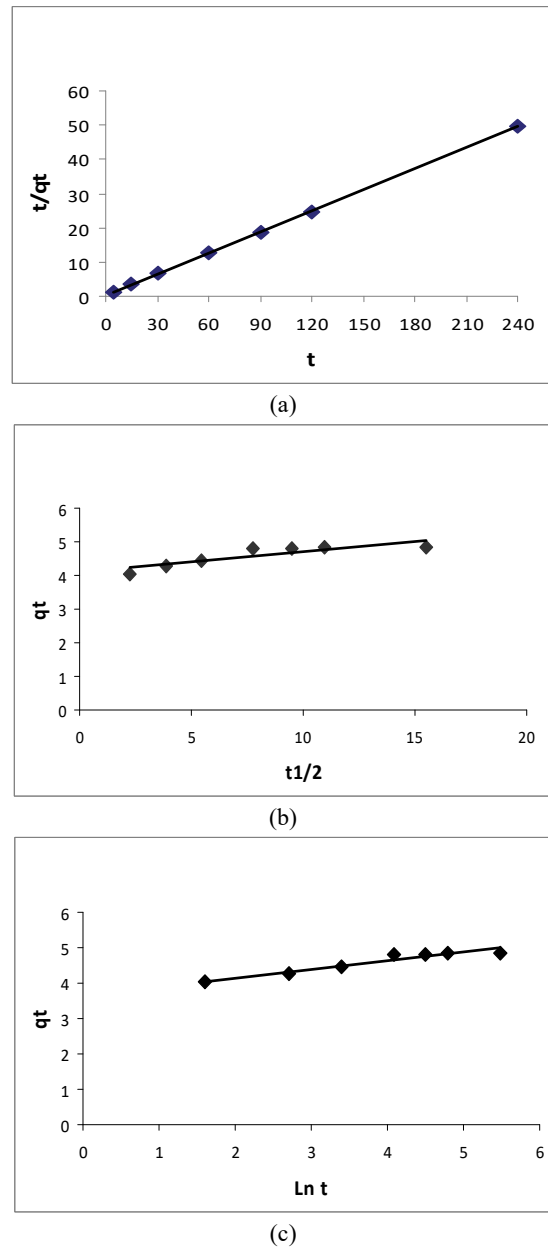


Fig. 8. (a) Linerized pseudo-second-order kinetics plots for malachite green adsorption; (b) Linerized Intraparticle diffusion kinetics plots for malachite green adsorption; (c) Linerized Elovich kinetic plots for malachite green adsorption

However, *AIC* would be a more sound method to compare the goodness of fit to Pseudo second-order, Intraparticle diffusion and Elovich kinetic models. Accordingly, *AIC* values to waste foundry sand were calculated for Pseudo second-order (8.68), Intraparticle diffusion (9.55) and Elovich (10.14) kinetics, respectively. Having a smaller *AIC* value to waste foundry sand suggests that Pseudo second-order kinetic model is more likely to be a better fit. By comparing the *SSE* of these models in the three kinetic systems, it seems that Pseudo second-order kinetic model was the best

fit although the SSE for the Intraparticle diffusion is very similar.

Table 6. The kinetics constants for the removal of malachite dye by waste foundry sand

<i>Kinetics</i>	<i>Waste Foundry Sand</i>
<i>Pseudo-second-order</i>	
q_e (mg/g)	4.882
k_2 (g/mg min)	0.125
R^2	0.999
<i>Interparticle diffusion</i>	
C	4.080
k_{id}	0.063
R^2	0.750
<i>Elovich</i>	
β (g/mg)	0.242
α (mg/g min)	4214139.6
R^2	0.926

Table 7. Nonlinear regression for adsorption kinetic parameters

<i>Kinetics</i>	<i>Waste Foundry Sand</i>
<i>Pseudo-second-order</i>	
SSE	3.844
AIC	8.686
<i>Interparticle diffusion</i>	
SSE	4.575
AIC	9.556
<i>Elovich</i>	
SSE	5.145
AIC	10.143

3.9. Thermodynamic parameters

The adsorption standard free energy changes (ΔG°) are determined with the following (Eq. 16) (Alpat et al., 2008; Lin et al., 2008).

$$\Delta G^\circ = -R T \ln K \quad (16)$$

where R is the gas constant (8.314×10^{-3} kJ/K mol), T is the temperature (K), and ΔG° is the free energy of sorption.

The equilibrium constant was calculated from Eq. (17):

$$K = q_e / C_e \quad (17)$$

where q_e and C_e were the equilibrium concentrations of malachite green in solution and on the sorbent correspondingly.

The sorption distribution coefficient may be expressed in terms of enthalpy and entropy changes as a function of temperature (Eq. 18):

$$\ln K = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (18)$$

The enthalpy change (ΔH°) and the entropy change (ΔS°) can be calculated from a plot of $\ln K$ versus $1/T$. The values obtained were given in Table 8. The endothermic nature of process is well

explained by positive value of the enthalpy change. The negative value of free energy suggests that the adsorption process is spontaneous and the affinity of the adsorbent for the dye is indicated by the positive value of entropy.

Table 8. Thermodynamic coefficients for malachite green adsorption on waste foundry sand

	ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (kJ/mol K)
	20°C	30°C	50°C	70°C		
<i>Waste Foundry Sand</i>	-1.807	-4.092	-6.414	-7.196	28.999	0.107

4. Conclusion

The present study has examined the adsorption of malachite green from aqueous solution on waste foundry sand. The adsorption of malachite green was found to be dependent on contact time, adsorbent amount, pH, initial dye concentration and adsorption temperature. The percentage of removal increased with the increasing adsorbent amount, pH and contact time and decreased with increasing initial dye concentration.

The experimental results showed that adsorption behavior is described by Langmuir isotherm. The data indicate that the adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps. Thermodynamic study showed that the adsorption process was spontaneous and endothermic since ΔG° value was negative and ΔH° value was positive.

The present study concludes that waste foundry sand can effectively be used as an adsorbent for the removal of malachite green from wastewater. Moreover, re-using waste foundry sand as is attractive in terms of sustainable development, and allows the foundry industry to accrue savings through reduced disposal costs.

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