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Araştırma Makalesi

Adsorption of Malachite Green by An Agricultural Waste: Rice Husk

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Abstract

The main objective of this research was to investigate the adsorption of malachite green as a cationic dye on rice husk as an agricultural waste. Effect of initial dye concentration, pH and time was evaluated. The adsorption data were calculated Langmuir, Freundlich isotherm model and kinetics. Langmuir isotherm (Q_{max}=8.688 mg/g) is more fitted than Freundlich isotherm. Scanning electron microscope (SEM) results described that characterization of rice husk. Pseudo second order kinetic model fitted well for removal of malachite green. Thus, rice husk was using no-cost and effective adsorbent for adsorption of cationic dyes.

Anahtar kelimeler: Adsorption, malachite green, isotherm, kinetic, SEM

Tarımsal bir Atık Tarafından Malaşit Yeşilinin Adsorpsiyonu: Pirinç Kavuzu

Öz

Bu çalışmanın temel amacı, tarımsal bir atık olarak pirinç kavuzu üzerine katyonik bir boya olarak malaşit yeşilinin adsorpsiyonunun araştırılmasıdır. Başlangıç boya konsantrasyonu, pH ve zamanın etkisi araştırılmıştır. Adsorpsiyondan elde edilen verilerle Langmuir, Freundlich izoterm modelleri ve kinetikler hesaplanmıştır. Langmuir izotermi (Q_{max}=8.688 mg/g) Freundlich izoterminden daha iyi uyum sağlamıştır. Pirinç kavuzunun karakterizasyonu taramalı elektron mikroskopu (SEM) ile tespit edilmiştir. Yalancı ikinci derece kinetic model malaşit yeşilinin gideriminde uyum sağlamıştır. Sonuç olarak pirinç kavuzu katonik boyaların adsorpsiyonunda etkili ve maliyetsiz bir adsorban olarak kullanılabilmiştir.

Key words: Adsorpsiyon, malaşit yeşili, izoterm, kinetik SEM

Introduction

Dye materials are progressively being used in cosmetics, food, fabric, paper and photography industries with increasing population. Huge quantity of dyes is discharged into the water bodies with during dying process. These are pollute and toxic for aqueous environment. Many dyes are non-biodegradable and difficult to remove from aquatic environment (Noreen et al., 2020; Ishtiaq et al., 2020; Li et al., 2019; Abbas et al., 2019; Ghourbanpour et al 2019; Sharma and Kumar 2019; Lou et al., 2019). These dyes need to be treated. There are many technics for treatment of dyes effluents such as adsorption, chemical oxidation, coagulation and oxidation. However, adsorption is more attractive technic among them. In general, characteristic of dye wastewater is described in Table 1 (Gosavi and Sharma 2013). According to Table 1 there are three types of dye effluents such as chemical oxidation demand (COD), color intensity; low, average and high concentration.

Table 1. Characteristic of dye wastewater (Gosavi and Sharma 2013)

Category	COD (ppm)	BOD (ppm)	pH	Temperature (°C)
Low	460	100	10	31
Average	970	270	9	28
High	1500	500	10	28

The rice husk includes dry matter rice (20%–25%). Also, they are usually separated from rice. The rice husk is used for animal as an animal feed. A large amount of rice husks are burned an open environment. It can cause air pollution. Rice husk should be disposed of properly (Kalita et al., 2015; Johar et al.,2012). The rice husks have matchless properties such as high porosity, external surface area and lightweight. It is also used as a valuable material for industrial applications such as rubber, cements, coatings, absorbents, pigments (Leung et al., 2013; Moon et al. 2011).

In this research rice husk used an adsorbent for removal of malachite green by adsorption. Effect of dye concentration, pH and time was evaluated. The adsorption data were calculated Langmuir, Freundlich isotherm model and kinetics. SEM results described that characterization of rice husk. Hence, rice husk was using no-cost and effective adsorbent.

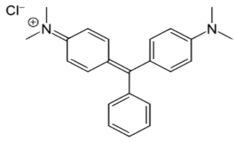
Material and Methods

Materials

Malachite green was obtained from Carlo Erba Reagent. Stock solution of malachite green was prepared in distilled water in room temperature. pH values were adjusted by addition HCl and NaOH (0.1 M). Properties of dye are given in Table 2. Figure 1 and Figure 2 described malachite green and rice husk respectively. Rice husks are shown in Figure 1.

Figure 1. Rice Husk

Table 2. Characteristic of Malachite green

Malachite green	
Molecular weight (g/mol)	364.90
Color	Green
λ_{max} (nm)	619
Dye purity	<90%
Chemical formula	$C_{23}H_{25}ClN_2$
Structure	

Adsorption Studies

Malachite green concentration was measured uv-vis spectrophotometer (Shimadzu UV 1208) in the wavelength of 619 nm. The surface morphological structures of rice husk was observed using SEM. The pH was measured in digital pH meters (WTW 82362 Weilheim). The solution was shaken by a mechanical shaker (VWR) during adsorption experiments.

Adsorption experiments were carried out in 250 mL erlenmeyer 0,3 g rice husk was added to the erlenmeyer including 30 mL of malachite green solution. The mixture was stirred by a shaker (VWR) at the constant agitation rate (200 rpm) and 25 ^{0}C. The dye solutions were centrifugation for separation from the adsorbent. The absorbance of dye was measured.

The removal efficiency of malachite green dye was calculated as follows, Eq. 1:

$$\text{Dye Removal } (\%) = \frac{C_o - C_t}{C_o} x100 \qquad (1)$$

C_o: The initial dye concentration (mg/L)

C_t: The dye concentration after sorption time t (mg/L) (Santos et al., 2013; Guo et al., 2003).

Results and Discussion

Characterization of Adsorbent

Investigation of surface characteristic by scanning electron microscope (SEM) image of rice husk before and after adsorption were given in Figure 2 and Figure 3 respectively. According to Figure 2 before adsorption rice husk has a curved structure. After adsorption rice husk has a flat structure (Figure 3).

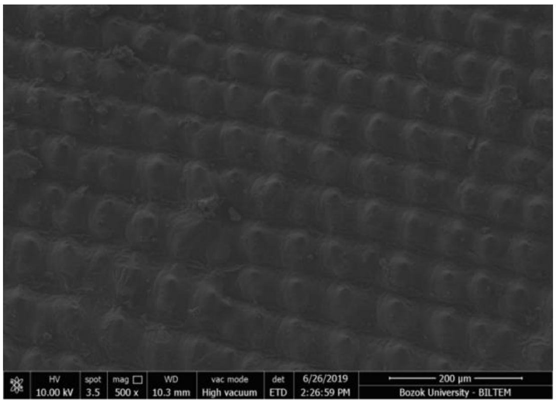


Figure 2. Rice husk before adsorption

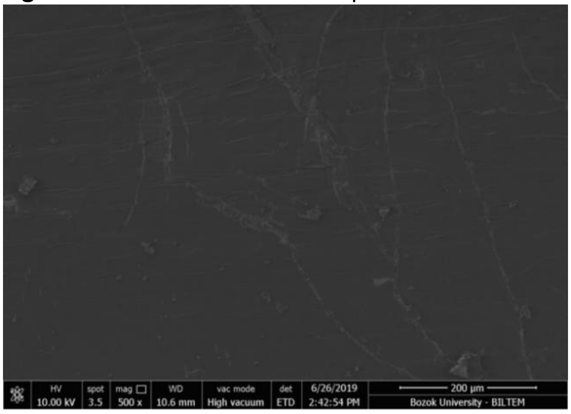


Figure 3. Rice husk after adsorption

Effect of pH

Five flasks containing 0,3 g of rice husk at initial pH values in the range from 2,6 to 10 at room temperature and 200 rpm for 24 hours. pH of dye solutions adjusted with HCl and NaOH**.** At first, maximum adsorption capacity increased with increased pH, after that it is stable (Figure4). The maximum adsorption capacity reached its highest value at 10. Similar results found that Gou et al., (2003).

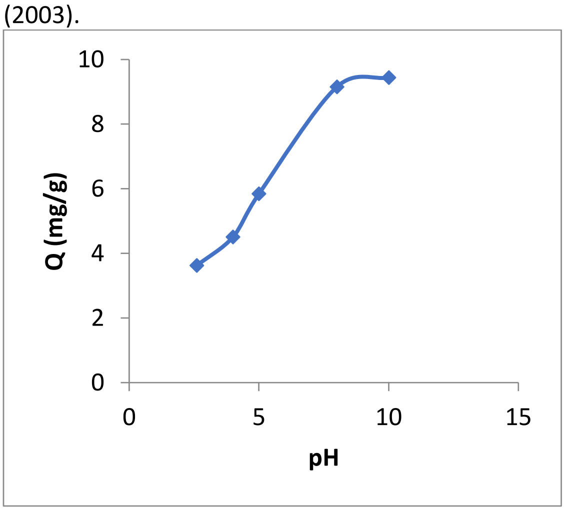


Figure 4. pH Effect (C=100 mg/L; m=0,3 g; T=25 ^{0}C; V=30 mL)

Effect of Concentration

The effect of the initial malachite green concentration on the adsorption capacity of the rice husk was also studied. The result is given in Figure 5 With increased initial malachite green concentration from 500 to 900 mg/L, the uptake amount of malachite green onto the resulting sample increased; over 600 mg/L, the adsorption amount was unchanged.

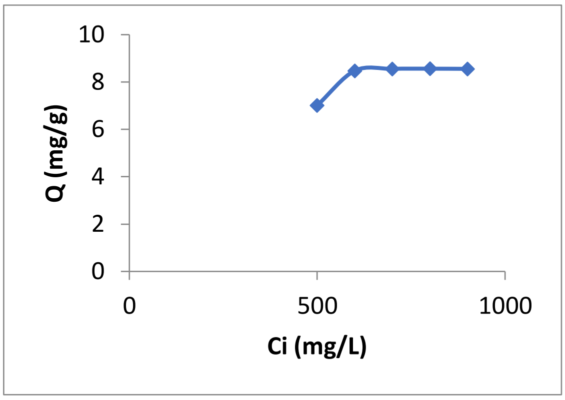


Figure 5. Concentration Effect **(**m=0,3 g; T=25 ^{0}C; V=30 mL)

Effect of Contact Time

The effect of contact time on adsorption of malachite green was investigated. The result was shown in Fig 6. The adsorption rapidly occurred. Similar results were found Leng et al, 2015 (Leng et al., 2015).

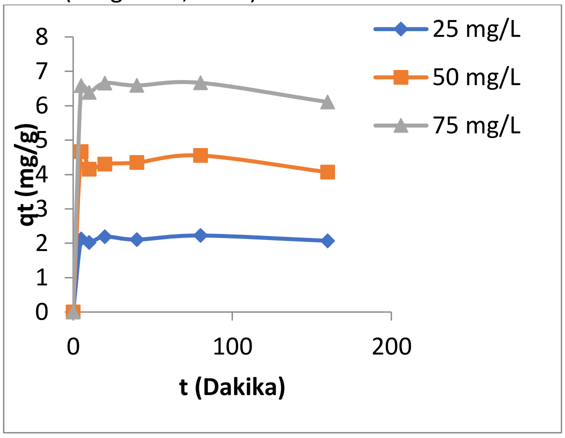


Figure 6. Effect of Contact Time

Adsorption Isotherms

The adsorption data of malachite green on rice husk were fitted by using Langmuir and Freundlich models (Figure 7-8, Table 3-4). The Langmuir isotherm had higher correlation coefficient (R^2) than the Freundlich isotherm.

Table 3. Langmuir Isotherm Coefficients

Adsorbent	Dye	K_L(L/g)	a_L	Qmax (mg/g)	R^2	References
Rice husk	Malachite green	0.769	0,088	8.738	0.9998	This study
Chemically modified rice husk	Malachite green	0.1597		12.16	0.975	(Chowdhury et al., 2011)
Rice husk ash	Brilliant green	0.3410		21.6024	0.9996	(Venkat et al.,2007)
Rice husk	Direct blue 19			8.555	0.968	(Saroj et al., 2015)
Rice husk ash	Indigo carmine	0.0131		29.2799	0.9854	(Lakshmi et al., 2009)

Langmuir isotherm equations are given as following equations (Hameed et al., 2008; Hameed 2008; Chowdhury et al. 2011):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e$$

$$q_e = \frac{Q_{max} a_L C_e}{1 + a_L C_e}$$

$$q_e = \frac{K_L C_e}{1 + a_L C_e}$$

Ce : The equilibrium concentration of adsorbate in solution after adsorption (mg/L)
qe :The equilibrium solid phase concentration (mg/g),
K_L (L/g); a_L (L/mg) : Langmuir constants.

Freundlich isotherm equation is given as following equations:

$$q_e = K_F C_e^{\frac{1}{n}}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

K_F (L/g) : The adsorption capacity
1/n : Intensity of adsorption

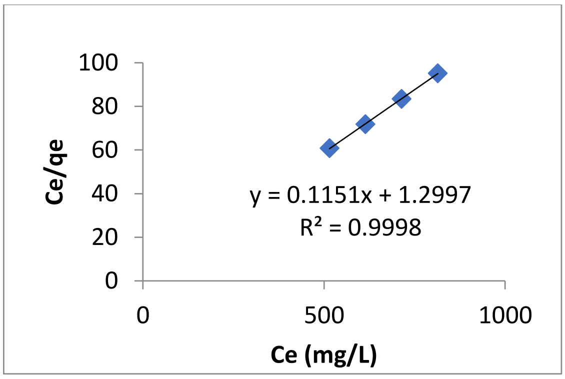


Figure 7. Langmuir Isotherm

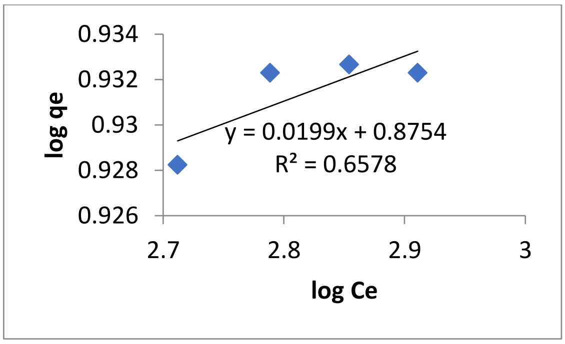


Figure 8. Freundlich Isotherm

Table 4. Freundlich Isotherm Coefficients

Adsorbent	Dye	n_F	K_F	R^2
Rice husk	Malachite green	50.251	7.505	0.6578

Adsorption Kinetics

Inraparticle diffusion, pseudo first order and pseudo second order models were calculated for adsorption of malachite green onto rice husk. However, we presented pseudo second order and intraparticle models because of the best fitted. As the adsorption kinetic parameters are shown in Table 5 and Figure 9, the high R^2 values, qe values indicate that Pseudo-second-order model described the kinetics of malachite green adsorption by rice husk.

Table 5. Pseudo second order kinetic coefficients

Initial dye concentration of Atermit Factory solid waste (mg/L)	q_e	$k_{2,ad}$	R^2
25	2.088	0.727	0.9988
50	4.113	0.176	0.9972
75	6.153	0.115	0.9982

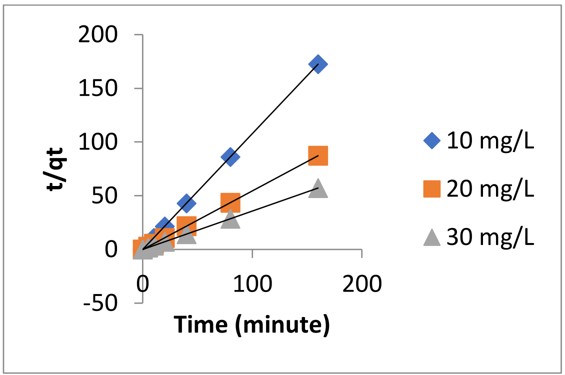


Figure 9. Pseudo Second Order Kinetic

We presented pseudo second order model is as follows (Ho and McKay, 1998):

$$\frac{t}{q_t} = \left[\frac{1}{k_{2,ad}q_{eq}^2}\right] + \frac{1}{q_{eq}}t$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt$$

qe: The amount of substance adsorbed per gram of adsorbent at equilibrium (mg/g)
qt: The amount of substance adsorbed by the gram of the adsorbent at any given moment (mg/g)
$k_{1,ad}$: Lagergren adsorption rate constant (dk^{-1})
k_{2ad}: Pseudo-second order adsorption rate constant (g/mg.dk)
k: Second order adsorption rate constant (g/mg.dk)
q_{eq}: Calculated amount of adsorbed substance (mg/g)
k_1, k_2 and k values are calculated by plotting log (qe-qt), t / qt and 1 / (qe-qt) values against the t value.

Also, the kinetic results were analyzed and fitted intra particle diffusion model (Table 6 and Fig 10). Fig 10 described that the adsorption of malachite green followed three-step processes. Similar results found that Leng et al., 2015 (Leng et al., 2015). Intra particle diffusion model equation is below (Weber and Morris, 1963):

$$k_p = q/t^{1/2}$$

q (mg/g): The amount of the adsorbed at time t,
kp: The intraparticle rate constant (mg/g min0.5).

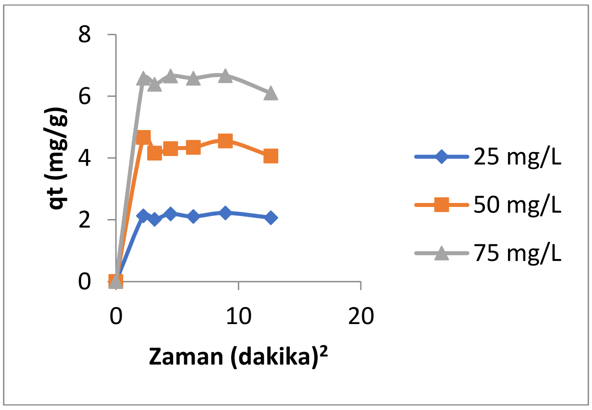


Figure 10. Intraparticle Diffusion Model

Table 6. Intraparticle Diffusion Model Coefficient

Initial Dye Concentration	k_{id} ($mg^{-1}dk^{1/2}$)	R^2
25	0.950	1
50	2.086	1
75	2.943	1

Conclusion

The paper was show that the investigation of adsorption of malachite green on rice husk as an adsorbent. Effect of pH, initial dye concentration and time was evaluated. The adsorption data were calculated Langmuir, Freundlich isotherm model and kinetics. Langmuir isotherm (R2=0,9998) is more fitted than Freundlich isotherm (R^2=0,6578). The data obtained from the adsorption experiment were used for kinetic studies. Pseudo second order kinetic model fitted well for adsorption of malachite green. SEM results described that characterization of rice husk. Hence, rice husk was using effective agricultural adsorbent for adsorption of malachite green.

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