Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 21, Sayı 3, 831-835, 2017

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 21, Issue 3, 831-835, 2017

DOI: 10.19113/sdufbed.46521

Adsorption of Methylene Blue and Methyl Orange By Using Waste Ash

Serpil SAVCI*[1], Mehmet Mert UYSAL[1]

[1]Bozok University, Engineering and Architecture Faculty, Biosystems Engineering Department, 66100, Yozgat

(Alınış / Received: 31.01.2017, Kabul / Accepted: 09.09.2017, Online Yayınlanma / Published Online: 13.10.2017)

Keywords
Waste ash,
Isotherm,
Desorption

Abstract: The adsorption in a batch system for methylene blue (MB) and methyl orange (MO) on waste ash were evaluated. The adsorption isotherms showed adsorptive maximum capacities for waste ash of MB and MO 40.983 mg g^{-1} 35.614 mg g^{-1} respectively. The equilibrium adsorption data were fitted by Dubinin-Radushkevic (D-R) adsorption isotherm model. The estimated values of adsorption energy, Ea, calculated from the D-R isotherm, for both MB and MO and waste ash systems were found to be 0.015 kJ mol^{-1} , 0.091 kJ mol^{-1} at room temperature respectively which implies that adsorption of both MB and MO on waste ash (0.3 g) is by physical adsorption. Waste ash and the dyes loaded waste ash were characterized by SEM. We studied reusability and it was found that the waste ash is stable and regenerable by 5 M HNO_3 without losing their activity. This research suggests that the waste ash can be an effective adsorbent for the removal of such acidic and basic dyes from aquatic solution.

Atık Kül Kullanılarak Methylene Blue ve Methyl Orange Adsorpsiyonu

Anahtar Kelimeler
Atık kül,
İzoterm,
Desorpsiyon

Özet: Methylene blue ve Methyl orange'nin atık kül üzerine adsorpsiyonu kesikli bir sistem ile değerlendirilmiştir. Adsorpsiyon izotermleri, atık kül için maximum adsorpsiyon kapasitesini methylene blue ve methyl orange için sırasıyla 40.983 mg g^{-1} 35.614 mg g^{-1} olarak göstermiştir. Dengedeki adsorpsiyon verilerinden Dubinin-Radushkevic (D-R) izoterm modeli de tanımlanmıştır. Dubinin-Radushkevic (D-R) izoterm modelinden hesaplanan adsorpsiyon enerjisi Ea, oda sıcaklığında methylene blue ve methyl orange için sırasıyla 0.015 kJ mol^{-1} , 0.091 kJ mol^{-1} olarak hesaplanmıştır. Bu da atık kül üzerine (0.3 g) methylene blue ve methyl orange adsorpsiyonunun fiziksel adsorpsiyon olduğunu ifade etmektedir. Atık külün boya yüklü ve boya yüksüz görüntüleri SEM ile karakterize edilmiştir. Yeniden kullanılabilirlik çalışmaları da yapılmış ve 5 M HNO_3 ile atık külün aktivitesini kaybetmediği ve yenilenebilir olduğu belirlenmiştir. Bu çalışma atık külün sulu çözeltilerden asidik ve bazik boyaların gideriminde etkili bir adsorban olduğunu önermektedir.

1. Introduction

Considering the run out of water resources in one day, water pollution and control is a very important in recent years. Dyes are one of the most common pollutants in the world. Even though the dyes discharged to the receiving environment constitutes only a small portion of water pollution, it is undesirable, especially in developed countries for aesthetics and ecology. Also, Dyes may spread toxic and carcinogenic metabolites in anaerobic conditions. Dyes can be treated by physical and chemical methods to prevent pollution in the aquatic environment. However, cost of these methods is extremely high. Sludge can be produced in some of these methods. In order to eliminate the color of the wastewater is a need for alternative methods. Adsorption is the most common methods for the removal of dyes from wastewater. In addition to it is well known process to treatment pollutants from aqueous media and investigations have been deeply sustained for the efficient process. Active carbon is the most preferred adsorbent because of high adsorption capacity. In recent days, more economical and environmentally friendly adsorbents have been used instead of activated carbon [1-2]. In this article, adsorption of MB and MO from aqueous solution on waste ash investigated as a function of initial pH level, initial dye concentration, and contact time by batch system. Langmuir, Freundlich and Dubinin

*Corresponding author: serpil.savci@bozok.edu.tr

Radushkevich isotherm models, kinetic and thermodynamic studies calculated for the adsorption of MB-MO by using waste ash.

2. Material and Method

2.1. Chemicals

MO ($C_{14}H_{14}N_3NaO_3S$ molecular weight 327.34 g/mol/l) and MB ($C_{16}H_{18}N_3ClS$ molecular weight 319.85 g/mol/l) were selected as an adsorbate. MO and MB were purchased from (Carlo Erba Reagent) Arkim Company in Turkey. Waste ash was obtained from a sugar factory in Yozgat in Turkey . The 1000 ppm stock solution of dye was prepared. Same studies were conducted for MO. The maximum wavelengths are 467 nm and 665 nm for MO and MB respectively.

2.2. Experimental studies

Adsorption studies were performed in 100 mL Erlenmeyer Flasks including 0.3 g of waste ash with 30 mL of MB and MO dye solutions. All the adsorption experiments were done at room temperature (25°C) via batch method. The solution was shaken by a mechanical shaker (VWR) at the constant agitation time (150 rpm) during 4 hours. Then the supernatant was centrifuged at 4000 rpm and 10 minutes in a centrifuge (Hettich Zentrifugen) after the batch tests. The absorbance's of MB and MO were measured at maximum wavelength by UV–VIS Spectrophotometer (Shimadzu UV 1208).

For the contact time experiments, the initial dye concentrations were varied from 100 to 1200 mg/L. The incubation time was tested in a time from 5 to 240 min. All experiments were repeated twice. The adsorption amount of MB and MO were calculated as follows, Eq. 1:

$$\text{Amount of adsorption (Q)} = \frac{(C_o - C_t)V}{m} \qquad (1)$$

C_o is the initial dye concentration (mg/L) whereas C_t is the dye concentration after adsorption, V dye volume (mL), m adsorbent mass (g) [3].

3. Results

Figure 1 shown that SEM images of unloaded and dye loaded of waste ash. A rough surface morphology appears in the SEM photographs of waste ash. The dye uptake capacity has increased because of surface characteristics [3-4]. After the adsorption, as seen in Figure 1.b, a large number of pores are filled with large amount of dyes.

3.1. Effect of initial dye concentration

According to the results, both MB and MO removal efficiency decreases whereas the amount adsorbed were increased with the increase in dye concentration (100-1200 mg/L). Similar results were found by Sait et al (2014). MB is adsorbed by volcanic ash in their study [5]. Figure 2. described that effect of initial concentration of dyes molecules on the adsorption amount. According to the the figure, the adsorption amount of dyes molecules increased with increasing initial dyes concentration then reach plateau value at higher concentration.

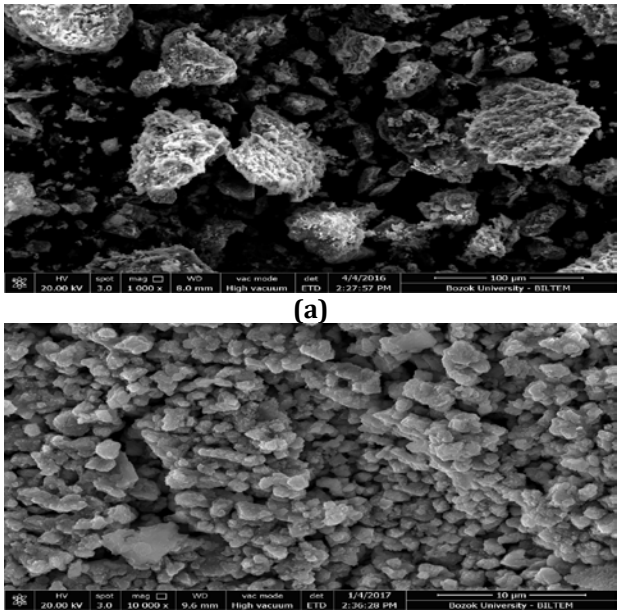

Figure 1. SEM images of unloaded (a) and dye loaded (b) waste ash

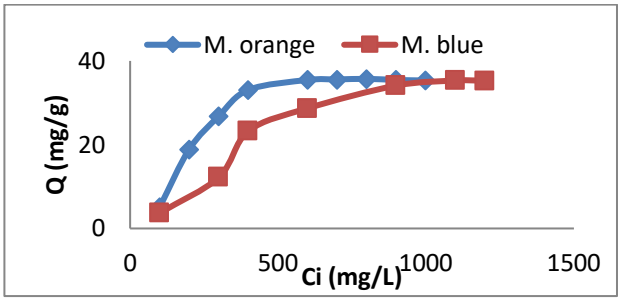

Figure 2. Effect of initial concentration of dyes molecules on the adsorption amount.

3.2. Effect of pH

The adsorption capacity as function of the initial pH value was studied at a fix concentration 100 mg/L, over a pH range from 2.6 to 10. The adsorption capacity of the waste ash was higher under acidic conditions in Fig 2. Maximum adsorbent quantity of 5.112 mg/g was achieved at pH 5 and minimum adsorbent quantity of 1.33 mg/g was obtained at pH=10 for MO. In addition to, maximum adsorbent quantity of 9.511 mg/g was achieved at pH 4 and minimum adsorbed quantity of 2.51 mg/g was obtained at pH=2.6 for MB. Saha et al (2010) studied adsorption of methyl orange onto chitosan. They found the most suitable pH is among the observed pH ranging from 4.0 to 9.0 [6]. Figure 3 shows effect of

pH on MB and MO removal isotherm of dye adsorption. The adsorption increased with the increase of pH from 4 to 5. After that it decreased with the increase of pH n then reached a plateau value.

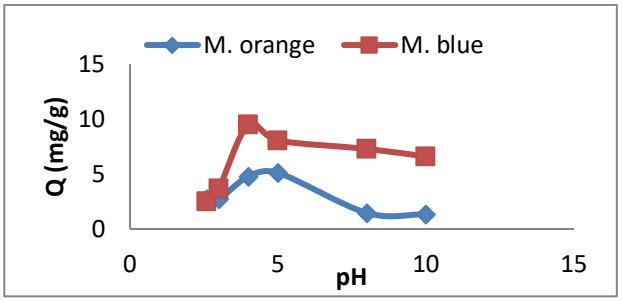

Figure 3. Effect of pH on MB and MO Removal Isotherm Of Dye Adsorption

3.3. Effect of contact time

The effect of contact time on adsorption of both MB and MO were investigated and the results were shown in Figures 4 and 5. Figure 4 shows variation of specific adsorption with time for MB. It shows that the waste ash has a high initial adsorption rate for dyes.

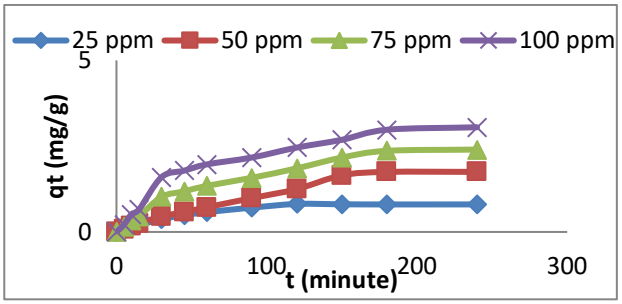

Figure 4. Variation of specific adsorption with time for MB (W=0.3 g, pH=4, V=30 mL, T= 25 ^{0}C)

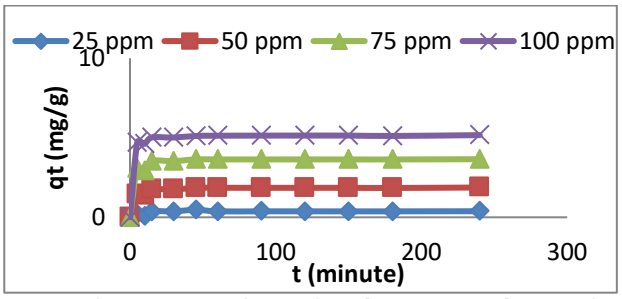

Figure 5. Variation of specific adsorption with time for various initial dye concentrations for various M. orange concentrations (W=0.3 g, pH=5, V=30 mL, T= 25 ^{0}C)

3.4. Adsorption isotherms

The adsorption of MB and MO onto waste ash was applied to Langmuir, Freundlich and Dubinin-Radushkevich (D-R) Isotherm Model (298 K). The three models constants and correlation coefficients for adsorption of MB and MO are shown in Table 1. E_a (energy) is useful for estimating the type of adsorption [7-8]. According to Table 1., estimated values of adsorption energy, Ea, was calculated from the D-R isotherm, for both MB and MO and waste ash systems were found to be 0.015 kJ mol^{-1} , 0.091 kJ mol^{-1} at room temperature respectively which implies that adsorption of both MB and MO on waste ash (0.3 g) is by physical adsorption.

Table 1. Isotherm parameters obtained from equilibrium models

Langmuir	Parameter (unit)	Methylene blue	Methyl orange
	K_L (L/g)	0.323	15.243
	a_L (L/mg)	7.881*10^{-3}	0.428
	Qmax(mg/g)	40.983	35.614
	R^2	0.9988	0.9998
Freundlich Isotherm	n_F	3.782	31.847
	K_F	6.153	29.302
	R^2	0.970	0.780
Dubinin-Radushkevich	q_m	35.103	35.591
	E_a	0.015	0.091
	R^2	0.9396	0.9784

Comparison of adsorption capacity of MB and MO onto some adsorbent in literature was given Table 2.

Table 2. Comparison of adsorption capacity of MB and MO onto some adsorbent in literature

Adsorbent	Dye	Q_{max} (mg/g)	References
Oil Shale Ash	MB	250	[9]
Baggase bottom ash	MB	142.54	[10]
Fly ash	MB	2.85	[10]
Cow dung ash	MB	5.31	[10]
Coal fly ash (0.01 NaCl)	MB	16.6	[11]
Coal fly ash	MB	12.7	[11]
Bioler fly ash	MO	249.9	[12]
Waste ash	MB	40.983	This study
Waste ash	MO	35.614	This study

Figure 6 shows Langmuir adsorption parameters for methylene blue and methyl orange. The adsorption behavior of waste ash fit Langmuir Model.

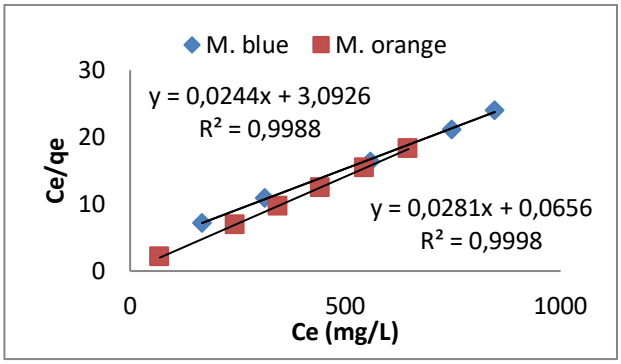

Figure 6. Langmuir isotherm parameters for MB and MO.

3.5. Kinetic study

Lagergren-first-order model, pseudo-second-order kinetic model and intraparticle diffusion model were used to evaluate adsorption kinetics. Figures 7 and 8 represents pseudo second order rate plot for MO and MB respectively. The system was adjusted to a pseudo second order kinetic model.

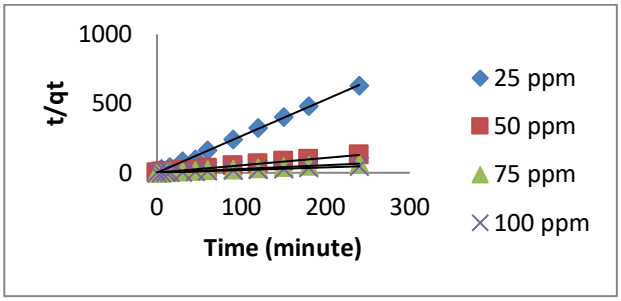

Figure 7. Pseudo second order kinetic model for methyl orange

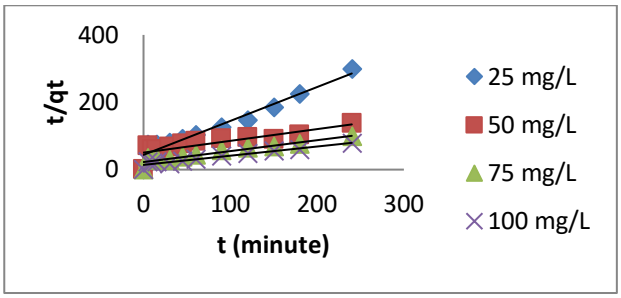

Figure 8. Pseudo second order kinetic model for methylene blue

3.6. Studies of reusability

Acid solution (5 M HNO_3) was used regeneration for waste ash, after that waste ash was used in dyes removal by adsorption. Waste ash is dried. Acid solution (5 M HNO_3) are added (30 mL) in a conical flask. Then the solution were shaken for 24 h. The waste ash were filtered and washed with distilled water until reach neutral pH. Waste ash reaching neutral pH was used in desorption experiments. Same procedure was repeated five times. Methylene Blue adsorption capacity of waste ash after adsorption/desorption cycle (Ci=100 ppm, T=25 ^{0}C, t=1 h pH=4) was shown in Figure 9. M. orange adsorption capacity of waste ash after adsorption/desorption cycle (Ci=100 ppm, T=25 ^{0}C, t=1 h pH=5) was shown in Figure 10.

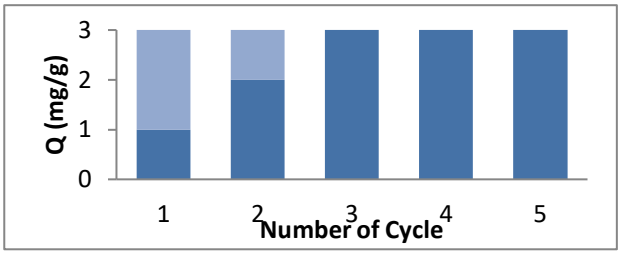

Figure 9. Methylene Blue adsorption capacity of waste ash after adsorption/desorption cycle (Ci=100 ppm, T=25 ^{0}C, t=1 h pH=4)

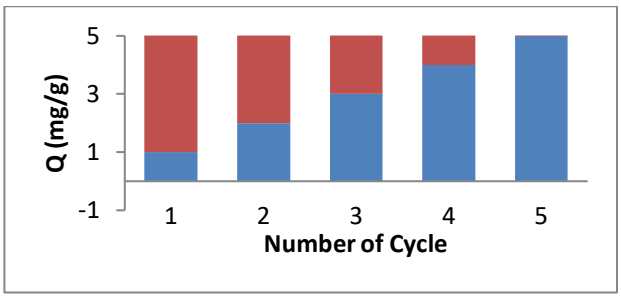

Figure 10. M. orange adsorption capacity of waste ash after adsorption/desorption cycle (Ci=100 ppm, T=25 ^{0}C, t=1 h pH=5)

4. Discussion and Conclusion

The adsorption of MB and MO on waste ash has been studied. The equilibrium experiments results shown prosperous adsorption and were better fit by Langmuir model in compared to the other models. Scanning electron microscopy (SEM) of the waste ash represent surface morphology which made it clear that waste ash is a good adsorbent. The pseudo-second order kinetic model equation was well described for kinetics (Higher R^2). The regeneration of waste ash without losing its original activity is found at least five cycles.

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