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Research article/Araştırma makalesi

Removal of a toxic basic dye-malachite green from aqueous solution by *Onopordum turcicum* Danin as natural biosorbent

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Abstract

Biosorption of malachite green (MG) was studies using natural origin adsorbent *Onopordum turcicum* Danin. Batch adsorption studies were carried out to evaluate the potentiality of *O. turcicum* for the removal of malachite green dye from wastewater, on different parameters such as pH, adsorbent dose, contact time and initial MG concentration. The effective pH was 8.0 for adsorption of MG by the biomass. The equilibrium isotherm was analyzed with the Langmuir and Freundlich models of adsorption. The biosorption data of MG on *Onopordum turcicum* Danin was fitted with Langmuir model with a maximum adsorption capacity was 1110.1 mg/g. The acquired results show that *O. turcicum* was effective in removal of MG dye from aqueous solution.

Key words: *Onopordum turcicum,* dye removal, biosorption

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Doğal biyosorbent olarak Onopordum turcicum Danin tarafından sulu çözeltiden toksik bir bazik boya-malakit yeşili uzaklaştırılması

Özet

Bu çalışmada doğal kaynaklı olan *Onopordum turcicum* Danin bitkisi adsorban olarak kullanarak, Malakit yeşil (MG) boyasının solu ortamdan uzaklaştırılması çalışılmıştır. Bitkinin potansiyel MG boya uzaklaştırma özelliklerini araştırmak amacıyla, pH, adsorban miktarı, temas süresi ve başlangıç MG konsantrasyonu gibi değişik parametrelere göre değerlendirilmiştir. MG boyasının *O. turcicum* biyokütle tarafından adsorlanan en etkin pH'sı 8.0 olarak tespit edildi. Adsorpsiyon izotermi ise Langmuir ve Freundlich adsopsiyon modeli kullanılarak analiz edildi. Langmuir izotermine göre adsopsiyon kapasitesi 1110.1 mg/g olarak bulundu. Elde edilen sonuçlara göre, *O. turcicum* bitkisinin MG boyasının sulu çözeltiden uzaklaştırabilme özelliğine sahip olduğu görülmektedir.

Anahtar kelimeler: *Onopordum turcicum,* boya uzaklaştırma, biyosorpsiyon

1. Introduction

The use of synthetic dyes in textile industry is increasing rapidly, and as a result, the release of dye contained wastewaters in the environment does not only contaminate the ecological environment but also puts the lives of all the aquatic living creatures in danger.

Malachite green (MG) is a cationic water soluble dye, often used in textile, ceramic, paper, leather, and paint industry. It also used for insecticide and preservative of aquatic products (Raval et al., 2016). But the dye is dangerous even toxic to aquatic life when it discharged to water without any treatment. In previous reports indicated that the MG dye reduced to leuco-MG in animal tissue which is acting as tumor promotor (Mittal 2006). Therefore, it is vital important to remove these dye molecules from water environment before their disposal (Iqbal and Ashiq, 2007).

A variety of methods have been developed over the years for the removal of textile dyes in waste water, among which there are aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation,

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filtration and reverse osmosis (Kumar, 2007; Doğan et al., 2009). However, all of the methods were not successful on removal of dyes from wastewater because of the reasons such as high cost, complexity of implementation and incompleteness. Therefore, it is important to find out more effective, easily available and costless biosorbents (Guari et al., 2015; Rahmat and Ali, 2016). In this context, our research mainly focused on evaluating the adsorption capacity of *O. turcicum*, its possible use on removal of malachite green dye from wastewater, to find out more affordable and environmental-friendly bio- adsorption.

2. Materials and methods

2.1. Chemicals and Instrumentation

All the chemicals used in this study are analytical grade. MG was obtained from Riedel-de Haen. Multi rotator, Biosan R 24 was employed for the effective mixing of sorbent and solution. MG stock solution was prepared by dissolving the appropriate amount in extra pure water. Then the working solution of MG was prepared by diluting stock solution to the desired concentrations and measured at 615 nm by UV-1600 spectrophotometer (Shimadzu, Japan). The pH measurement of solutions was carried out using the pH meter (Metler, USA). All solutions were prepared in ultra-pure water. pH of solutions was adjusted by Britton Robinson Buffer (boric, acetic and phosphoric acid, each of 0.04 M) and base (0.2 M of NaOH) solutions.

2.2. Plant materials and preparation of adsorbent

The plant material used in this study was collected from Sivas city in Turkey. Then the leaves were dried in shade for two weeks and the spines on the edges of the leaves were cut off. Before use, the leaves were crushed into coarse powder and sieved through 40- 60 mesh size sieve. The sieved particles were waited in the deionized water for about 12h, washed several times with deionized water and ethanol then dried at 50°C in an oven

Figure 1. A: General view of *O. turcicum* in natural habitat; B: Leaves of *O. turcicum*

2.3. Biosorption studies

Equilibrium experiments were performed by contacting 100 mg of *O. turcicum* dried leaves with 50mL of 50 mg/L MG solution at pH 8. A mixture of bioadsorbent and MG solution in conical flasks were shaken in a multi rotator (Biosan R 24) with a constant speed of 100 rpm. After reaching equilibrium (20 min), the absorbance of MG in supernatant was measurement by UV-VIS spectrophotometer (Shimadzu Brand UV-1600) at a maximum absorbance wavenumber 615 nm after a proper dilution.

The calibration plot which is produced from standard MG serial solution was used to calculate the final concentration of MG dye. The percent removal of MG was calculated by using the following formula:

$$removal\,\% = \frac{C_0 - C_f}{C_0} x100$$

Where, C_0 is the initial MG concentration in mg/mL, C_f is the equilibrium MG concentration in mg/ mL.

2.4. Bioadsorbent characterization

In order to characterization study on *O. turcicum* dried leaves of before and after adsorption of MG dye, scanning electron microscopy (SEM) studies were performed on a Tescan Mira 3XMU with an Oxford EDS analysis system. As can be seen from Figure 2, surface morphology of *O. turcicum* leaves had changed after biosorption of dyes.

The remarkable difference of SEM images of *O. turcicum* leaves before and after biosorption of dyes was the surface roughness. MG dyes are adsorbed on porous of *O. turcicum* leaves and among layers.

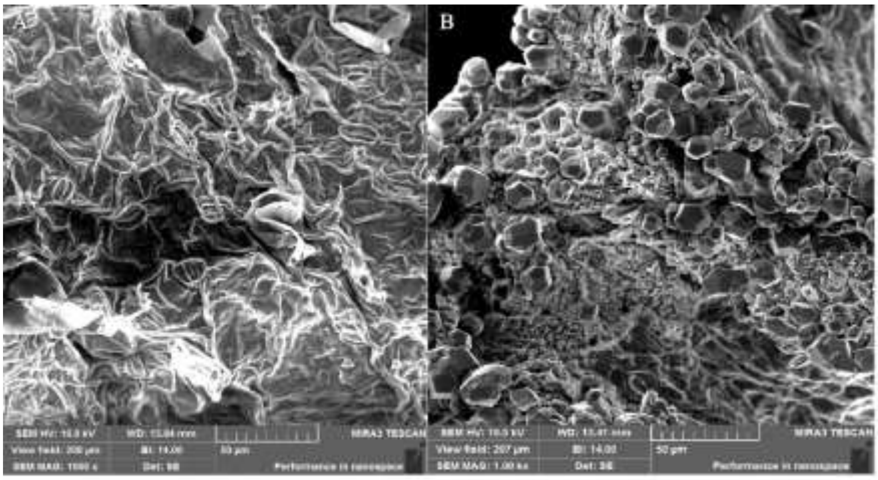

Figure 2. SEM images of *E. O. turcicum leaves a*: before biosorption, B: after biosorption of MG

Point of Zero charge (pH_{pzc})

The surface charge on *O. turcicum leaves* was obtained by means of batch equilibrium procedure by measuring the point of zero charge as experimental results. In brief, 100 mg of biosorbent was introduced to 50 mL of solution with different pH (1-10, adjusted with 0.1 M HCI acid and 0.1 M NaOH). After shaking 24 hours, the final pH values were measured with pH meter. The ΔpH value was calculated from the difference between intial and final pH. A plot of ΔpH vs. pH was used for determination of point of zero chage. The value of pH correspondence to ΔpH= 0 was taken as point of zero charge (Haddad et al. 2013) Point of zero charge was found as pH 5.0. At higher pH ranges (pH>5.0) surface of *O. turcicum leaves* is negatively charged. Therefore, cationic species were more feasible to biosorption on to *O. turcicum leaves* at this range. Point of zero charge of *O. turcicum leaves are* given Figure 3.

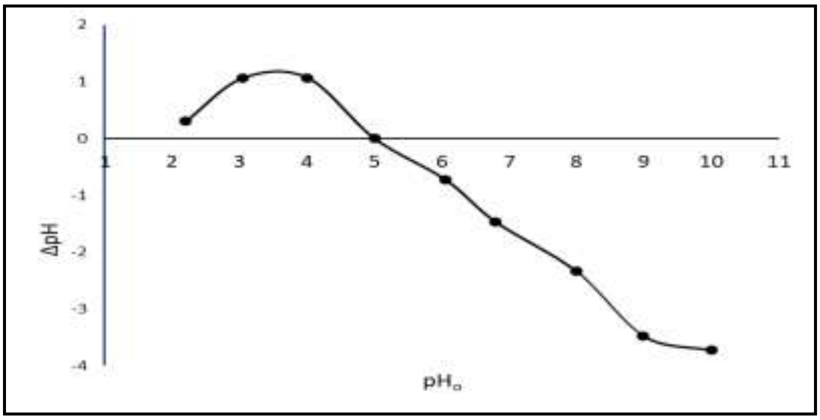

Figure 3. Point of zero charge of *O. turcicum leaves*

3. Results

3.1. Effect of pH on the dye adsorption

To examine an effect of pH on the dye adsorption, the pH values of the dye solution-bisorbent mixture were adjusted with addition of BR buffer. After equilibration reached to sufficient, the equilibrium pH values and dye concentrations were measured and the adsorbed amounts of dye by bioadsorbent were calculated. As can be seen from Fig. 4, the adsorption of Malachite Green increased with pH value after pH=7, adsorption remained almost unchanged. The bioadsorbent had maximum dye adsorption (≥ 95 %) over the pH range of 7-10. The biosorption process could be explained by the electrostatic interactions between the negatively charged surface and the positively charged molecule (MG^+) in the medium because the MG uptake increased with increase in initial pH (Ayed et al. 2009; Tsai and Chen, 2010).

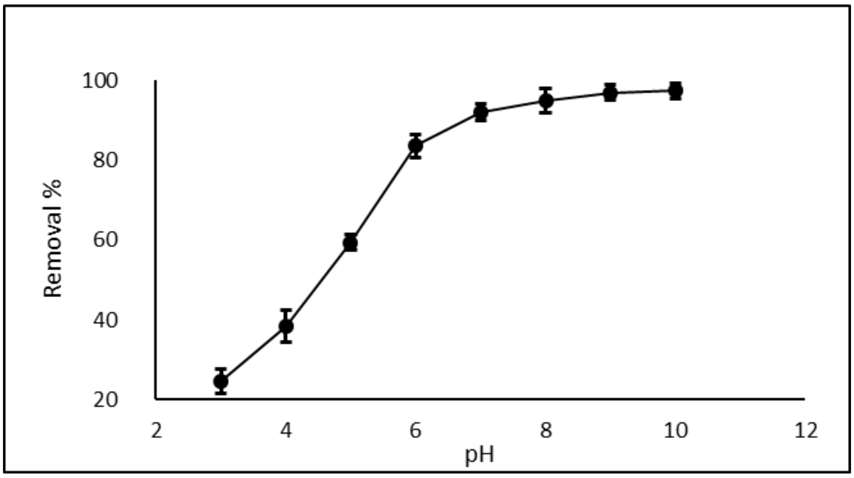

Figure 4. Effect of pH on the removal of MG dye solution

3.2. Effect of initial dye concentration

The influence of initial concentration of malachite green in the solutions on the rate of adsorption on *O. turcicum* dried leaves was studied. The experiment was performed at fixed adsorbent dose (0.1g/50 mL) in the test solution at different initial concentrations of malachite green (50, 100, 150, 200, 300, and 500 mg/L). Maximum dye removal (≥ 95 %) was achieved at 30 min. Figure 6A is shown the UV-VIS spectrum of 50 mg/L MG before and after biosorption in *O. turcicum* at 5, 10 and 15 min, respectively. Photographs of the same solutions are given in Figure 6B.

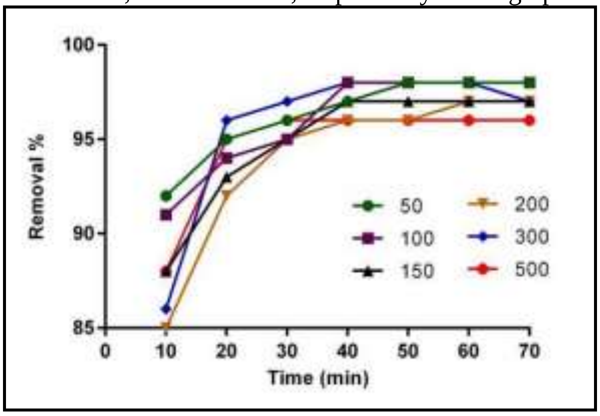

Figure 5. Effect of initial dyes concentration on the adsorption of malachite green on *O. turcicum* leaves (adsorbent dose=0.1g/50 mL, pH=8.0)

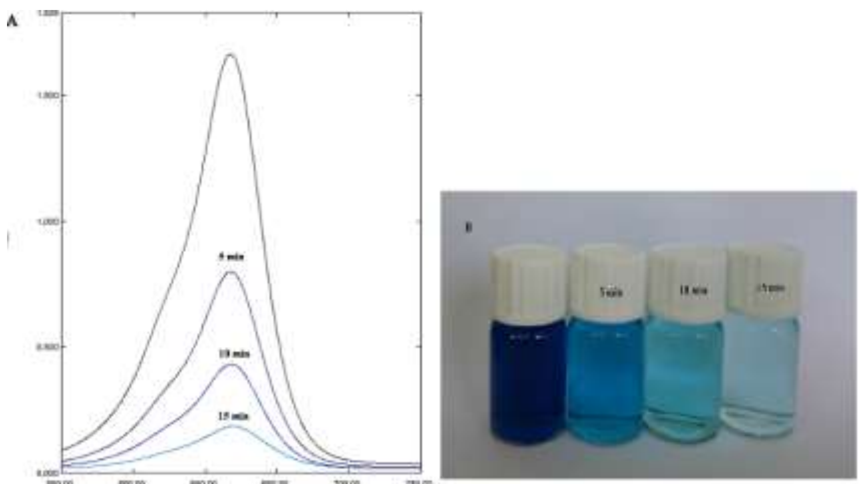

Figure 6. UV spectrum of 50 mg/L MG solution with time after absorbtion by *O. turcicum* leaves (A) and the image of the MG solution (B)

3.3. Effect of the biosorbent amount

The adsorption of malachite green on *O. turcicum* dried leaves was studied by altering the quantity of adsorbent (25, 50, 75 and 150 mg) in the test solution while keeping the other parameters such as dye concentration (50 mg/L), room temperature and pH=8.0 constant for 30 min. The adsorption was increased from 93% to 97% as the biosorbent dose was increased from 25 mg to 150 mg at equilibrium time.

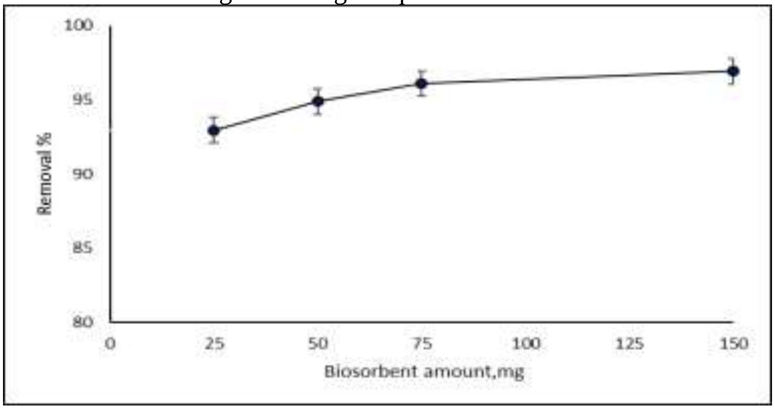

Figure 7. Effect of biosrbent amount on the removal of MG dye solution

3.4. Effects of possible coexisting metal ions

The removal % of MG was studied in the presence of various metal ions such as Zn^{2+},Cd^{2+}, Pb^{2+}, Fe^{3+},Cr^{3+}, Ag^{+}, Ni^{2+}, Cu^{2+} with final concentration of 50 mg/L of and Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} with concentration of 250 mg/L. The ion solutions were added individually to 50 mL of dye solution which is containing 50 mg/L of MG and 100 mg of biosorbent. As can be seen from the Table 1. No significant removal differences were found in the presence of metal ions in textile wastewater.

Table 1. Tolerance limits for interference ions on the determination of U(VI)

Ions	Recovery % ,U(VI)
Zn^{2+}	96.4 ± 0.3
Cd^{2+}	96.5 ± 0.6
Pb^{2+}	96.0 ± 0.8
Fe^{3+}	93.4 ± 0.3
Cr^{3+}	93.4 ± 0.2
Ag^{+}	95.2 ± 0.6
Ni^{2+}	96.1 ± 0.2
Cu^{2+}	95.2 ± 0.8
Ca^{2+}	98.1 ± 1.0
K^{+}	97.1 ± 0.1
Mg^{2+}	97.2 ± 0.5
Na^{+}	96.5 ± 0.4
A*	95.8 ± 0.5

* Mixture of all the metal ions, (Zn^{2+},Cd^{2+}, Pb^{2+}, Fe^{3+},Cr^{3+}, Ag^{+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}.

3.5. Adsorption isotherms

The adsorption isotherms widely used for understanding the situation of the adsorption and its mechanisms. There are currently most used two classical models namely Langumir and Freundlich equation, are used for explaining these isotherms. The Langmuir sorption isotherm is used for sorption of a pollutant from a liquid medium, while the Freundlich isotherms applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules (Crini et al., 2007)

The Langmuir equation is given as follows:

$$Q_e = \frac{Q_{max} K C_e}{1 + K C_e}$$

Where Qe is the amount of MG dye per mass of adsorbent (mg/g); Q_{max} is the maximum adsorption capacity (mg/g); Ce is the equilibrium MG liquid phase concentration (mg/L) and K is a Langmuir isotherm constant that is related with adsorption rate (Wawrzkiewicz and Hubicki, 2010).

Langmuir equation can be presented in as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{K Q_m}$$

The Freundlich isotherm is used for describing heterogeneous systems and the equation of Freundlich is expressed as follows (Zhou et al., 2016) (Robinson et al., 2002):

$$Q_e = K_f {C_e}^{1/n}$$

where Qe is the equilibrium MG dye concentration on adsorbent (mg/g), Ce the equilibrium dye concentration in solution (mg/l), K_f is the Freundlich constant (l/g), 1/n is a constant related with adsorption intensity (Kannan et al., 2013).

Freundlich isotherm can be expressed in the linear form as follows by taking logarithms of the former equation:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

the plot of ln Qe versus lnCe was employed to make the intercept equal to ln K_f and the slope of 1/n.

The experimental data demonstrated that, the biosorption mechanism for MG were suited with Langmuir model with a correlation constant of > 0.9998. The Q max value was found as 1110.1mg/g for MG as given in Fig 8. The n value calculated from Freundlich isotherm is 2.9 and this indicated the favorable biosorption of MG on *O. turcicum*. The calculated isotherm parameters for both Langmuir and Frendlich model are summarized Table 2.

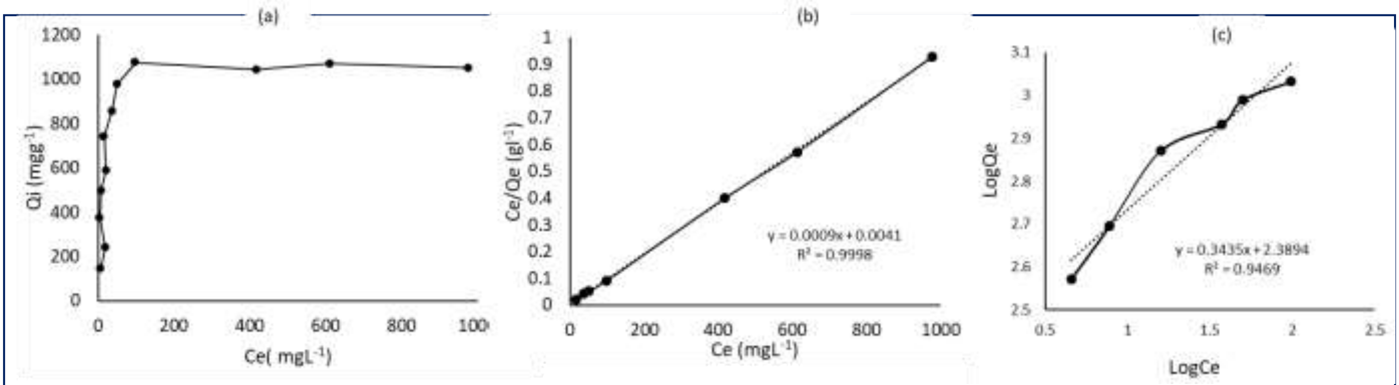

Figure 8. Isotherms of adsorption of MG dye on adsorbent at room temperature (a); Langmuir isotherm linear plots (b); Freundlich İsotherm (c);

Table 2. Langmuir and Freundlich isotherm Parameters

Dye	Langmuir Parameters			Freundlich Parameters		
	Q_{max}(mg/g)	K (L/mg)	R^2	K_f (L/mg)	n	R^2
MG	1110.1	0.219	0.9998	245.13	2.9	0.9469

4. Conclusions and discussion

It was found that the dried leaves of *O. turcicum* can be used for adsorption of malachite green dyes from aqueous medium. The adsorption was highly dependent on pH, initial dye concentration and adsorbent mass. *O. turcicum* is a commonly grown plant in Anatolia of Turkey, so it is easily available in the countryside. Therefore, the use of these costless materials by dyeing unit is recommended for removal of dye in wastewater. The maximum sorption capacity was 1110.1 mg/g, which has a considerable rapid and high removal capacity than the other biosorbents suggested for the removal of MG dye from wastewater (Table 2). The adsorption of MG dye increased with increasing pH. In separate experiment, the reusability of adsorbed *O. turcicum* leaves with MG dye, also can be used one more times because its adsorption capacity almost unchanged after first adsorption of the dye. *O. turcicum* is recommended for the treatment of basic wastewater because of its higher removal capacity in alkaline aqueous solutions.

Table 3. Comparison on removal capacity of bioadsorbents on MG dye with literature

Adsorbent	**q_{max} (mg/g)**	**Reference**
Hydrilla verticillata	91.97	(Rajeshkannan et al. 2010)
Neem sawdust	4.354	(Khattri, 2009)
Polygonum orientale Linn	556.00	(Wang et al. 2010)
Coco peat	276.80	(Vijayaraghavan et al. 2016)
Groundnut shell	222.22	(Malik et al. 2007)
Lemon peel(Type2)	51.418	(Kumar, 2007)
Coffee bean	55.3	(Baek et al. 2010)
Chlorella-based biomass	9.775	(Tsai and Chen, 2010)
O. turcicum	1110.1	This study

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