RESEARCH ARTICLE
Bull Biotechnol (2021) 2(1):1-5
https://doi.org/10.51539/biotech.734889 Jurnal homepage: www.dergipark.org.tr/biotech

Bulletin of Biotechnology

Crystal violet removal study with natural and biochar prina from aqueous solutions

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Received : 09/05/2020
Accepted : 01/04/2021

Abstract: In this study, as industrial waste, prina was used as an adsorbent substance with its natural and thermally modified form. The prina used in the study was taken as waste material from an olive oil factory in Ayvalık, Turkey. In this study, the removal possibilities of the toxic effect of crystal violet dye found in various industrial wastewaters with prina adsorbent were investigated. By using the pyrolysis method at 600 °C, the biochar form of prina was obtained. Natural and biochar prina and crystal violet (CV) dye have been tried under different adsorption conditions. For this purpose, experiments were carried out at different prina dosages, initial dye concentrations and contact times. The highest removal efficiencies are around 75% in natural prina, while the biochar is around 99% in prina. Also, concentration studies were applied to Langmuir and Freundlich adsorption isotherm models. As a result of the isotherm study, it was seen that the adsorption mechanism was suitable for Freundlich isotherm model. The contact time removal studies were applied to pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models, and adsorption was found to be fit with the pseudo-second-order kinetic model. According to the experiment results, it was observed that the thermal treatment caused a significant increase in the removal efficiency. It was found that it is an efficient adsorbent material that can be used to remove the CV dye from the aqueous solutions.

Keywords: Adsorption; biochar; crystal violet; dye removal; isotherms; kinetics.

1 Introduction

Olive and oil industry have great economic importance in many Mediterranean countries. According to the Olive And Olive Oil Report For 2018 has approximately 95 million olive trees and 658 000 hectares of olive groves in Turkey and 100.000-250.000 tons of annual oil production in Turkey (T.C. Ministry of Commerce 2019). Olive oil is produced from olives using hydraulic presses or modern horizontal axis centrifuges, and both processes produce highly polluted wastewater and or solid waste. Solid wastes are generally known as "olive cake" or "olive rice". The olive waste consists of cellulose, lignin, amino acid, protein and uronic acids, and oily waste and polyphenolic compounds. These components contain many functional groups. These include carboxylic, hydroxylic and methoxy groups, and many of fixed anionic and cationic functional groups. Prina is usually swallowed through controlled spreading to agricultural soil. Only a small amount of this sediment is used as a natural fertilizer in animal foods, a heat energy source and additives. It is not believed that most of these applications have significant economic value. It is, therefore, useful to find other applications for such an agro-industrial solid waste. (Akar et al. 2009)

Prina, obtained from olive oil factories, is an agricultural product produced in Mediterranean countries. It is exposed during the extraction of olive oil. Make up 6-8% residual olives, 20-33% water, 59-74% seed. Olive oil factories produce about 15-22 kg of olive oil and 35-45 kg of prina from 100 kg of olives in olive oil extraction processes. There are many studies on pollutant removal from wastewater with prina. (Malkoç et al. 2006)

Crystal Violet is an inexpensive dyestuff used for silk, leather, paper dyeing and many different purposes. Besides, culture staining is also frequently used in microbiology. It has a very dense and sticky dye. When the crystal violet dissolves in water, it significantly reduces the light transmittance and disrupts the natural ecolgical balance. Crystal violet is a tri-phenylmethane dye. Crystal violet dye is a water-soluble, toxic organic paint that causes serious health problems and environmental pollution (Cheruiyot et al. 2019).

In general, the dyes are divided into three classes: cationic or basic dyes, anionic or acidic and nonionic or disperse dyes. Cationic dyes, in particular, are primarily applied in the textile industry as water-soluble, cost-effective and widely distributed in the relevant market. Synthetic origins and

aromatic structure dye molecules are generally very stable and cannot be eliminated in nature; also, they are often toxic and suspected to be carcinogenic. It is, therefore, interesting to remove dyes from industrial wastewater. Even though many different physical, chemical, electrochemical and biological methods have been proposed to remove dyes from polluted waters, adsorption has significant advantages over them due to good efficiency, versatility and relatively low costs for removing organic substances well as considerable flexibility against high pollutant load. (Toumi et al. 2018).

The adsorption process takes place in the presence of an adsorbent layer that binds the molecules through physical forces, ion exchange and chemical forces. Adsorption is a treatment process that removes all dye molecules and leaves no parts in wastewater (Rangabhashiyam et al. 2013).

In this study, prina was used in the color removal of crystal violet dye prepared in the laboratory. The availability of the prina in waste status in terms of pollution removal has been investigated and it has been emphasized that it can be a valuable and inexpensive substance.

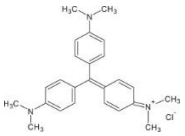
2 Materials and Method

2.1 Materials

The prina used in this study was obtained from an olive oil factory in Ayvalık, Turkey. The prina was washed three times with distilled water. The washed prina was dried in a 103 °C oven for 24 hours. The dried prina was crushed with a Waring brand blender and sieved at 30 mesh. This 30 mesh prina was used as a natural adsorbent.

For the preparation of biochar prina adsorbent, 30 mesh natural prina was operationalised to pyrolysis. Biochar production was carried out with a Uniterm brand high-temperature reactor. The reactor provides a stable temperature through mantle heating. The reactor chamber consists of titanium alloyed stainless steel material. There are inlet and outlet section that provides nitrogen gas flow in the reactor. The gas outlet part was passed through ice water and cooled. The pyrolysis process was carried out at a slow pyrolysis rate of 5 °C/min at 600 temperature, under 100 mL/min nitrogen gas flow, 1 hour waiting time conditions. Pyrolysis conditions were determined by testing similar pyrolysis studies in the literature and selecting average values (Qiu et al. 2018; Demiral and Şamdan 2016; Georgieva et al. 2020; Kaya et al. 2020). 6.38 g biochar was obtained from 20 g of raw prina placed in the steel reactor. The obtained biochar is ready for use in the experiment as adsorbent.

Table 1 Some properties of crystal violet dye

CAS No.	Chemical	Molecular Weight	C.I. Name	Molecular Structure
548-62-9	$C_{25}H_{30}ClN_3$	407.979 g/mol	Basic Dye	

Crystal violet ($C_{25}H_{30}ClN_3$) was chosen for adsorption studies. The wastewater sample was prepared as a synthetic aqueous solution with a concentration of 1000 mg/L with CV solid dye. 1000 mg/L stock solution was prepared by dissolving correctly weighed amounts of CV in 1000 mL distilled water. Table 1 shows some of the properties of CV dye.

2.1 Method

Adsorption studies were carried out with natural and biochar prina under different adsorption conditions to reduce the CV concentration. Adsorption experiments run to determine maximum removal conditions; at different prina dosages (2-4-8-20 g/L), at contact times (1-15-30-60-90-120-240 min) and initial CV concentration (50-100-200-400-600-800 mg/L). General adsorption conditions were carried out at 25 mL CV solution volume, 8 g/L walnut shell dosage, 50 mg/L initial CV concentration and 60 min contact time.

The prepared solutions were mixed with an Innova model 2000 brand platform shaker at 175 rpm for 60 minutes. After mixing, samples were centrifuged at 9000 rpm for 10 minutes then, after adsorption, CV concentrations were measured with a Thermo brand Aquamate model UV spectrophotometer at 590 nm wavelength.

Also, the initial concentration study was applied to adsorption Langmuir and Freundlich isotherm models. The contact time study was applied to pseudo-first-order, pseudo-second-order model and intra-particle diffusion kinetic models.

Removal efficiency values after adsorption calculated by Equation 1;

$$E(\%) = \frac{C_0 - C_e}{C_0} \text{ x } 100 \qquad (1)$$

There; E (%) is percent removal efficiency, C_0 (mg/L) initial CV concentration, and C_e (mg/L) CV concentration after adsorption.

Also, adsorption capacities were calculated in all adsorption studies. Adsorption capacity is the amount of adsorbate that the adsorbent's unit mass (or volume) can adsorb. The adsorption capacity (qe) is formulated in Equation 2;

$$q_e(mg/g) = \frac{C_0 - C_e}{m} xV \qquad (2)$$

Where; C_0 and C_e (mg/L) are the initial concentration and equilibrium concentration of dye solution, respectively, V (L) is the volume of dye solution and m (g) is the mass of adsorbent.

3 Results and Discussion

3.1 Effect of adsorbent dosage on removal

To determine the optimum dosage, natural and biochar prina was subjected to adsorption process at 2-4-8-20 g/L adsorbent dosages, 25 mL sample volume, 50 mg/L initial CV concentration for 60 minutes contact time. Removal

efficiencies and adsorption capacity (qe) values were calculated for natural and biochar prina.

The results of the dosage study are given in Figure 1. In general, removal efficiency also increased with increasing dosage of adsorbents. However, removal efficiencies at 8 g/L and 20 g/L are very close to each other, therefore 8 g/L was chosen as the optimum adsorption dosage. Looking at the graph, biochar prina has 20-25% higher removal efficiency compared to natural prina. The selected dosage is at 8 g/L, the yields are 75.85% and 98.14% for natural and biochar prina, respectively. With increasing adsorbent dosage, removal efficiency has also increased. The yields started to stabilize after the 8 g/L dosage. This is due to the increase in the available surface area and the number of adsorption areas. The higher the adsorbent dosage, the more binding area is available for the CV to be taken up to the prina surface. The selected dosage is at 8 g/L, the yields are 75.85% and 98.14% for natural and biochar prina, respectively.

Vithalkar and Jugade (2020) have carried out a study of CV removal with chitosan-coated bentonite. Similar to this study, in the adsorbent dosage versus removal efficiency experiments, they obtained a constantly increasing removal efficiency despite the increasing adsorbent dosage. Wang et al. (2020) carried out CV removal studies with activated sugarcane adsorbent. The adsorbent dosage versus removal efficiency study obtained 90% removal efficiency at the adsorbent dosage of 3.33 g/L and the removal efficiency remained constant at increasing adsorbent dosages.

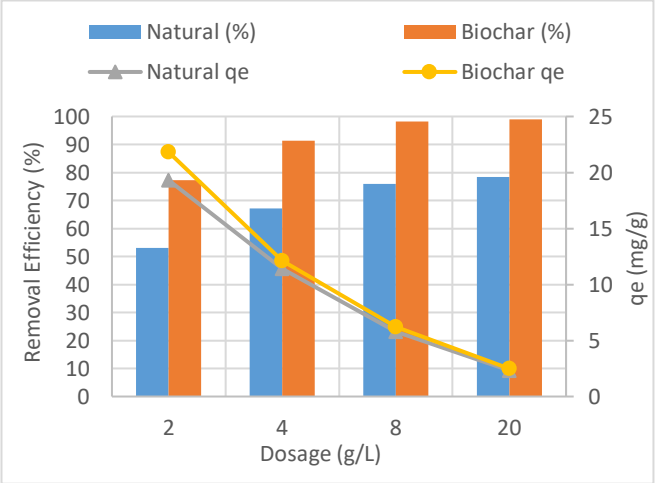


Fig. 1 Effect of dosage natural and biochar prina on removal efficiency

3.2 Effect of contact time on removal

To determine the effect of contact time on adsorption, experiments were conducted under general adsorption conditions for 1-15-30-60-90-120-240 minutes.

Figure 2 gives the results of removal efficiency and adsorption capacity. According to the results, biochar prina has much higher removal efficiency than natural prina. The biochar prina quickly reached equilibrium from the first minute and with rising contact times, removal efficiency was very low. The natural prina reached equilibrium after 60 minutes. Removal efficiencies obtained with natural and biochar prina in 60 minutes selected as the optimum contact time were obtained as 75.44% and 99.10%, respectively.

Vithalkar and Jugade (2020) in their contact time study with chitosan-coated bentonite CV removal efficiency, reached the equilibrium time at 20 minutes. After this period, they obtained an almost constant removal efficiency. Priya et al. (2020) studied CV removal with active tropical fruit peels and commercial activated carbon. In their contact time study, they stated that the adsorption reached equilibrium within 30 minutes. Besides, they obtained the highest removal efficiency as 98% with commercial activated carbon adsorbent.

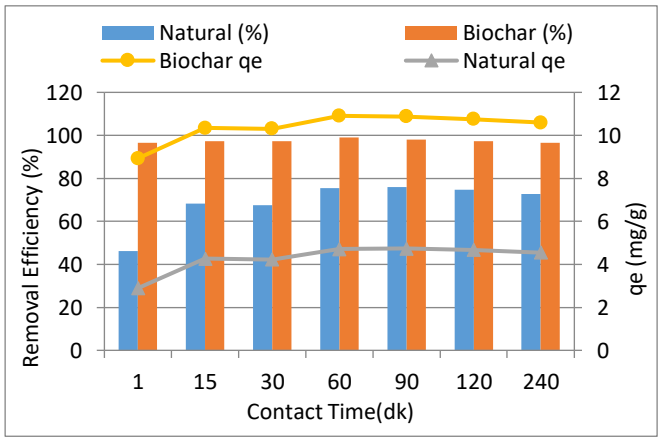


Fig. 2 Effect of contact time natural and biochar prina on removal efficiency

3.3 Effect of initial concentration on removal To determine the effect of the initial CV dye on adsorption, removal studies were carried out at the initial concentrations of 50-10-200-400-600-800 mg/L.

The results of concentration experiments are given in Figure 3. Biochar prina has high removal efficiency as well as other dosage and contact time studies. The removal efficiency was almost constant at lower initial concentrations, while a reduction was observed after 400 mg/L initial concentration. Therefore, an initial concentration of 50 mg/L was chosen for use in adsorption experiments. The highest removal efficiency was calculated as 75.85% and 98.14% for natural and biochar prina, respectively.

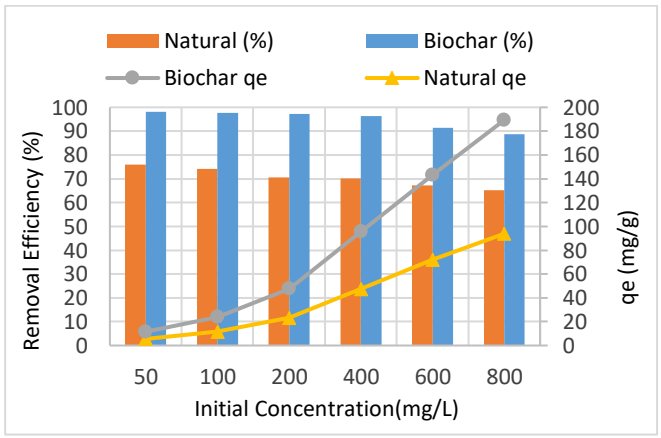


Fig. 3 Effect of initial concentration natural and biochar prina on removal efficiency

Wang et al. (2020), in their removal study with active sugarcane adsorbent against the initial CV concentration, achieved a partially decreasing removal efficiency with increasing initial concentration. They also stated that similar to this study, the adsorption capacity (q_e) increased rapidly from the 200 mg/L concentration to the 1000 mg/L concentration.

3.4 Adsorption isotherms

Initial concentration experimental data were applied to Langmuir and Freundlich isotherm models to determine the CV dye adsorption mechanism on natural and biochar prina.

The Langmuir equation is valid for single layer adsorption on the surfaces of a finite number of identical areas, and the Langmuir isotherm equation can be written as Equation 3;

$$\frac{C_e}{q_e} = \frac{1}{(q_m x K_L)} + \frac{C_e}{q_m} \quad (3)$$

There, qe, the amount adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_m and K_L are the Langmuir constants related to the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively. (Rangabhashiyam et al. 2018).

The Freundlich isotherm is an empirical model that is based on adsorption on the heterogeneous surface area. The Freundlich equation is used to describe heterogeneous systems and is as in Equation 4 in logarithmic form.

$$\log q_e = \log K_F + \frac{1}{n\ x\ \log C_e} \quad (4)$$

There, qe is the amount of dye adsorbed per adsorbent of dye adsorbent (mg/g) is the equilibrium concentration in Ce (mg/L), K_F and n are empirical Freundlich constants, indicative of adsorption capacity and adsorption density, respectively (Dönmez and Aksu 2002).

Correlation coefficients with Langmuir and Freundlich parameters are given in Table 2. The suitability of adsorption to the isotherm model is expressed by the proximity of R^2 to 1. Accordingly, natural and biochar prina R^2 values were found to be suitable for the Freundlich model as 0.927 and 0.998, respectively.

Table 2 Correlation coefficients of isotherm models

Isotherm Model	Parameter	Natural Prina	Biochar Prina
Freundlich	k_F (L/g)	1.34	5.56
	n	0.75	1.27
	R^2	0.927	0.983
Langmuir	q_{max} (mg/g)	133.3	169.4
	K_L (L/mg)	0.010	0.028
	R^2	0.218	0.886

3.5 Adsorption kinetics

In order to research the adsorption mechanisms and potential rate-controlling step of CV removal, three standard kinetic models, such as the pseudo-first-order model (Lagergren 1898), pseudo-second-order model (Ho and McKay 1998) and intra-particle diffusion model (Tan et al. 2009). The correlation coefficients (R^2) were represented in Table 3.

Table 3 Parameters of adsorption kinetic models

Kinetic Models	Parameter	Natural Prina	Biochar Prina
Pseudo First Order	k_1 (min^{-1})	$6.67x10^{-3}$	$4606x10^{-4}$
	qe (mg/g)	2.07	6.30
	R^2	0.13	0.0018
Pseudo Second Order	k_2 (g/mg.dk)	11.58	0.29
	qe (mg/g)	4.59	6.04
	R^2	0.999	0.999
Intraparticle Diffusion	k_i ($mg/g.min^2$)	0.0985	0.0002
	C	3.53	6.09
	R^2	0.529	0.0003

Since the highest R^2 values are obtained in the pseudo-second-order kinetic model, adsorption is suitable for this model for both natural and biochar adsorbents. These results suggested that both physical and chemical adsorption might be involved in the adsorption process. Two consecutive stages could reason this phenomenon: the could be driven to access or into the pores of the adsorbent by the concentration gradient at the initial stage; after that, the CV ions did not diffuse into the pores of prina for further reactions until the surface functional sites were occupied fully. Based on this, CV's adsorption process in aqueous solution might only happen on the surface of prina and even the monolayer adsorption on the outer-sphere surface of complexes. To lend credence to this, focusing on the pseudo-second-order model.

4 Conclusion

Optimum adsorption conditions for CV removal with natural and biochar prina adsorbent were determined as 50 mg/L initial CV concentration, 8 g/L adsorbent dosage and 60 min contact time. The highest removal efficiencies obtained were 75.44% and 99.10% for natural and biochar prina, respectively. Likewise, the highest qe values were 93.86 mg/g and 95.43 mg/g for natural and biochar prina. These values are higher than in many studies in the literature. It has been observed that the adsorption mechanism fits the Freundlich isotherm model and pseudo-second-order kinetic model for both natural and biochar prina. The results obtained have shown that high-efficiency, cheap and abundant waste prina can be used as a suitable adsorbent in CV removal. Biochar prina has shown 20-50% higher removal efficiency than the natural form of prina. The high efficiency of dye removal is also of great importance in terms of turbidity. Therefore, thermal treatment is not an unnecessary step and the use of

biochar prina will provide much higher removal efficiencies. This study will contribute to such studies in the literature.

Authors' contributions: Sevda Esma Darama was interested in calculating the results, interpreting the data and arranging them according to the format. Özlem Uçar was interested in performing the experiments. Semra Coruh was interested in organizing the study.

Conflict of interest disclosure: Our work has not been carried out with any organization or employees.

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