



Biosorption of methylene blue and acid red 88 from wastewater by using peanut shell

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ABSTRACT

This study represents the removal of harmful dye substances from wastewaters by using a waste and cheap biosorbent. For this aim, peanut shell was used as a biosorbent for the removal of methylene blue and acid red 88 dyes. The effects biosorbent amount, initial dye concentration, pH, temperature, contact time and dye type on biosorption were studied. In the study, the highest removal of acid red 88 was found as 88% using dye solution of 200 ppm with 5.0 grams of peanut shell at contact time of 300 minutes. The highest removal of methylene blue was determined as 99% using dye solution of 200 ppm with 4.0 grams of peanut shell at contact time of 60 minutes. As a result of dye type, methylene blue which has a linear geometric structure has demonstrated a high removal than acid red 88. Biosorption isotherms for both dyes were found more consistent with the Langmuir model according to Freundlich model.

Keywords: Biosorption, peanut shell, methylene blue, acid red 88.

Yer fıstığı kabuğu kullanarak atıksudan metilen mavisi ve asit kırmızısı 88 boyasının biyosorpsiyonu

ÖZ

Bu çalışma atık ve ucuz bir biosorbent kullanarak atık sularadan zararlı boyar maddelerin uzaklaştırılmasını temsil etmektedir. Bu amaçla, yer fıstığı kabuğu metilen mavisi ve asit kırmızısı 88 boyalarının uzaklaştırılması için bir biosorbent olarak kullanıldı. Biyosorpsiyon üzerine biosorbent dozu, başlangıç boyar madde konsantrasyonu, pH, sıcaklık, temas süresi ve boya tipinin etkileri incelendi. Çalışmada, asit kırmızısı 88' in en yüksek uzaklaştırılması 300 dakikalık temas süresinde yer fıstığı kabuğunun 5 gramı ile 200 ppm'lik boya çözeltisi kullanılarak % 88 olarak bulundu. Metilen mavisinin en yüksek uzaklaştırılması ise 60 dakikalık temas süresinde yer fıstığı kabuğunun 4 gramı ile 200 ppm'lik boya çözeltisi kullanılarak % 99 olarak belirlendi. Boya tipinin bir sonucu olarak lineer bir geometrik yapıya sahip olan metilen mavisi, asit kırmızısı 88' den daha yüksek bir uzaklaştırma göstermiştir. Her iki boya için biyosorpsiyon izotermi Freundlich modeline göre Langmuir modeliyle daha tutarlı bulundu.

Anahtar Kelimeler: Biyosorpsiyon, yer fıstığı kabuğu, metilen mavisi, asit kırmızısı 88.

1. INTRODUCTION

Water is the most important vital resource for living beings in terms of life's existence in the earth. When the establishment and expansion places of the ancient civilizations were investigated, a water edge has been always preferred. As a result of the significance of water resources, wars have come to the fore, and the importance of freshwater resources has once again been revealed.¹ Due to both industrialization and rapid population growth in the world, existing water sources are subject to anthropogenic contamination. The damages caused by this pollution can cause non-reversible damages to the environment. One such way of water

pollution is a result of the dyes used in textile factories.² With the consumption of these dyestuffs, an enormous pollution can occur in the environment that can disrupt the ecological balance. Dyes are used for the colorization process of objects such as fabric and fibers in the textile industry. Moreover, these dyes are decomposed by biodegradable methods due to their molecular structure. Synthetic dyestuffs are used widely in textile, paint, paper and printing industries. Today, over 100,000 synthetic dyes are used commercially and 700,000 tons of dyes is produced annually.³ When the amount of dye production and remaining waste of dye after its usage are considered, it is evident that the removal of the colored wastewaters is essential for the preservation of the

environment. Beside the primary harm of the dyestuff pollution, there are many other side effects of the polluted colored wastewaters where the water resource becomes unfit for use as nourishment.⁴ Some dyes have mutagenic and / or carcinogenic effects. The lack of photosynthesis causes the amount of dissolved oxygen in the water to derogate so that the anaerobic microorganisms outcompete aerobic microorganisms, which results in the formation of malodorous compounds in the growth of anaerobic microorganisms in the environment. In addition, the lack of oxygen can create a significant danger for the lives of other living things that require oxygen.⁵⁻⁷ Many biological, physical and chemical methods are used for the treatment of wastewater containing dyestuffs. These methods can be listed as; anaerobic treatment⁸, coagulation–flocculation⁹, adsorption¹⁰, biosorption¹¹, ultrafiltration¹², electrocoagulation¹³, and ion exchange.¹⁴ The most common and most important of these methods is adsorption. It is based that certain molecules dissolved in liquid phase cling onto the surface of a solid substance. According to other conventional methods, adsorption technique have attracted interest in recent years because it provides an effective removal the pollutants from environment. Adsorption is economically reasonable and provides high quality product formation.¹⁵ The most used raw material in adsorption process is activated carbon also known as the widest adsorbent.¹⁶ As it has a highly porous structure, it has an adsorption capacity of between 500 and 1200 m² per gram of surface of activated carbon. For this reason, in many industrial processes, the activated carbon is seen to be used.¹⁷ However, active carbon is an economically disadvantaged adsorbent and it challenges researchers to find new, cheap, natural, and local adsorbents as alternatives to activated carbon. One of these alternatives, as proposed in this study, is peanut shell. Peanut is make peanut oil, butter, flour, and as a vegetarian protein resource, and are commonly harvested in global market to be consumed for nutritional purpose. Its annual production was over 43.9 million tons in 2014.¹⁸ Peanuts have a covering shell which is not appropriate for nutritional usage where it appears as a waste in the industries using peanuts.¹⁹ Hence, in this study, peanut shells are used as low-cost biosorbent material.

2. MATERIALS AND METHODS

In this study, a low-cost peanut shell was used as an biosorbent. Upon removal of methylene blue and acid red 88 dyes from the wastewaters by the usage of biosorbent, the effect of the biosorbent amount, contact time, dye concentration, pH, temperature, dyes type parameters were investigated. The results were calculated by measuring a UV-Visible spectrophotometer. The operations carried out in this aim are as follows:

2.1. Biosorbent preparation

The biosorbent which is in a state of waste after the consumption of peanuts, was firstly subjected to a washing process to minimize its chromaticity and then was applied to a drying process at 50°C in a thermal G11320SD oven. The dry peanut shells obtained after the dehydration process (there was a reduction in size), by the aid of emery paper, was pulverized in the context of expanding the surface area. In this direction, the biosorbent, which has become smaller in size, has been preserved by transferral into nylon plastic bags.

2.2. Preparation of colored wastewaters

First of all, artificial wastewaters are prepared in this direction. Distilled water was used as a solvent in the solutions, since water pollution is being investigated. For this reason, the stock solutions of methylene lue and acid red 88 of 800 ppm were prepared. Then, 50, 100, 200, 300 ppm solutions of methylene blue and acid red 88 dyes from the stock solutions were were prepares by diluting from stoch solutions. preserved in 100 mL HDPE containers for interaction with the biosorbent. methylene blue and acid red 88 were supplied from the local textile industry, AK-KIM Textile Industry in Yalova, Turkey. Their molecular structures are shown in Figures 1 and 2.

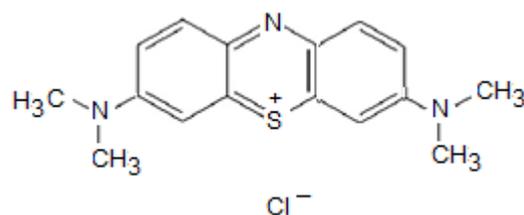


Figure 1. Methylene blue.

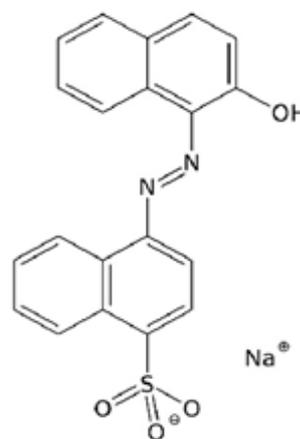


Figure 2. Acid red 88.

2.3. Application of adsorption experiments

In the case of carrying out the adsorption experiments, the previously prepared methylene blue dye and acid red 88 solution were interfaced with the biosorbent designated as Peanut Shell dust, which is stocked in plastic packages. 0.1, 0.25, 0.5, 1, 2, 4, 5 grams of adsorbents were used in the adsorption process. In the case of more homogenous dispersion of the mixture contained in 100 ml HDPE containers, the mixture was allowed to stand for 5 minutes as standard in all experiments. Then, all the solutions were rinsed at 110 rpm on a Thermal N11340 shaker at a variety of interaction time (0.25, 0.5, 1, 2, 4, 5 hours). Samples taken from the dye solution were initially centrifuged in Yuda 800D Centrifuge at 110 rpm to eliminate the residue particles and the samples were collected in closed test tubes. Then supernatants were analysed using UV-Vis spectrophotometer.

2.4. Analysis of experimental results

Shimadzu UV-Vis-2600 spectrophotometer was used to perform spectral scanning for methylene blue and acid red 88 dyes. As it is shown in Figure 3, the maximum absorbance values were read at 502 nm for acid red 88 and at 654 nm for methylene blue.

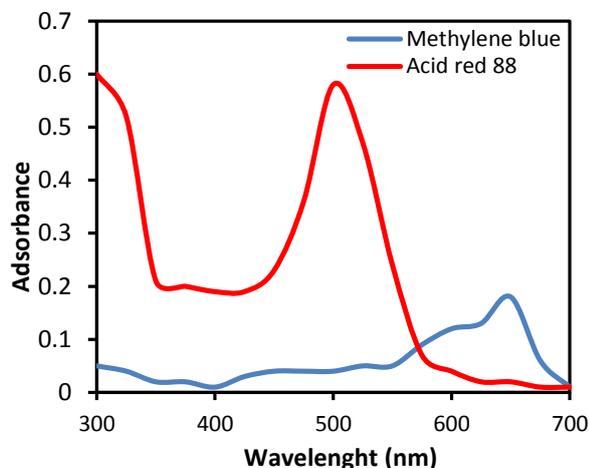


Figure 3. UV-Vis spectra of dyes.

In addition, in the measurements made with standard stock solutions, the R^2 value are found to be more than 0.99 as shown in Figures 4 and 5. Standard graphics in Figures 4 and 5 were used to determine the amounts of dyes removed by biosorbent.

2.4.1. Calculation of the biosorption capacity of biosorbent

When the system is in equilibrium during the adsorption process, the amount of substance adsorbed by

unit mass of biosorbent material was calculated as a function of temperature, and concentration. The amounts of dye adsorbed were estimated by using Eq. (1).

$$q_e = (C_0 - C_e) V / m \quad (1)$$

where q_e is the adsorption capacity of biosorbent (mg g^{-1}), C_0 is the initial concentration of dye (mg l^{-1}), C_e is the concentration of the dye adsorbed at the equilibrium (mg l^{-1}), V is the volume of solution (l), and m is the mass of the biosorbent (g).

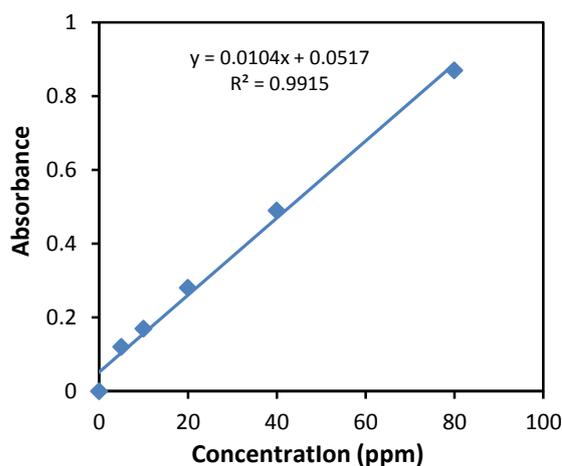


Figure 4. Standard absorbance graph of methylene blue.

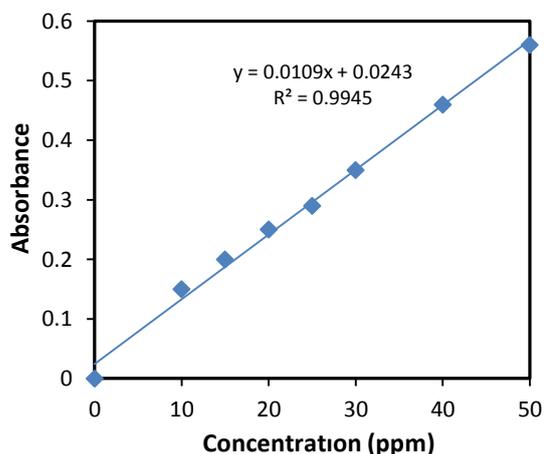


Figure 5. Standard absorbance graph of acid red 88.

2.4.2. Biosorption isotherms

The biosorption isotherm was studied according to the Langmuir and Freundlich isotherm models, which are used commonly.

The linear form of the Langmuir isotherm equation which indicates a homogenous adsorption, is given in Eq. (2),

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (2)$$

In the equation, q_m is the maximum adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration of dye in liquid phase (mg l^{-1}), K_L is Langmuir isotherm constant indicating adsorption energy. From the slope and intercept of the plot of C_e/q_e vs C_e , the values of q_m and K_L are obtained respectively.

The linear form of Freundlich isotherm equation which indicates a heterogeneous adsorption can be expressed in Eq. (3),

$$\ln q_e = \ln k + 1/\ln C_e \quad (3)$$

In this equation, C_e is the equilibrium concentration of dye remained in liquid phase (mg l^{-1}), and q_e is amount of dye that is adsorbed by unit biosorbent (mg g^{-1}). k and n are the Freundlich isotherm constants. k indicates biosorption capacity (mg g^{-1}), n indicates the intensity of biosorption. From the slope and intercept of the plot of $\ln q_e$ vs $\ln C_e$, the values of n and k are obtained respectively.

3. RESULTS AND DISCUSSION

3.1. The effect of dye type on biosorption

In order to determine the efficacy of the different type of the dyes, the working conditions was kept constant at room temperature, $\text{pH} = 7$, 4 grams of the biosorbent, and dye concentration of 200 ppm. When the graph in Figure 6 is examined, a higher removal rate is observed in the methylene blue dye than in the acid red 88 dye.

The most acceptable reason for the high removal of methylene blue that it has a more appropriate geometric shape than acid red 88. Molecular structures of the dyes are shown in the Figures 1 and 2. Due to its linear structure, methylene blue molecules have the ability to demonstrate better biosorption into the pores of the biosorbent.

On the other hand, methylene blue and acid red 88 have different wavelengths, where blue color has a larger wavelength than the red color. Thus, the color difference is a considerable factor to the removal difference between the dye samples. The concentration which reduced below near-zero levels in experiments with methylene blue reveals that the peanut shell dust has a great potential of adsorbing ability. According to Figure 6, this high removal rate take places at an interaction time of about 30 min. At this point, the interaction time should be kept in 30-60 minutes period in order to prevent the loss of energy.

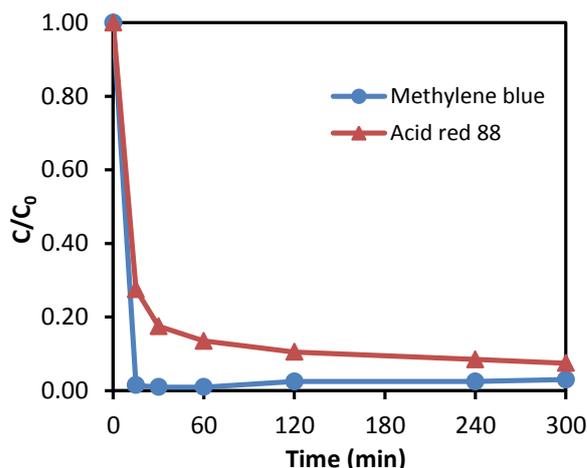


Figure 6. The effect of dye type on the biosorption of dyes (Dye concentration: 200 ppm, biosorbent amount: 4 gram).

3.2. The effect of initial dye concentration on biosorption

To examine the effect of the dye concentration on biosorption, the experimental conditions was kept constant at $\text{pH} = 7$, at room temperature, at the interaction time of 60 minutes, and 4 grams of biosorbent. According to Figure 4, the removal curve for acid red 88 dye stays at a lower level than the methylene blue removal curve. Therefore, when the type of dyes is examined, it appears that methylene blue dye has a higher adsorbing property. As a result of the interaction of the dyes with the peanut shell according to Figure 7, the highest removal is seen at 200 ppm for acid red 88, and 50 ppm for methylene blue.

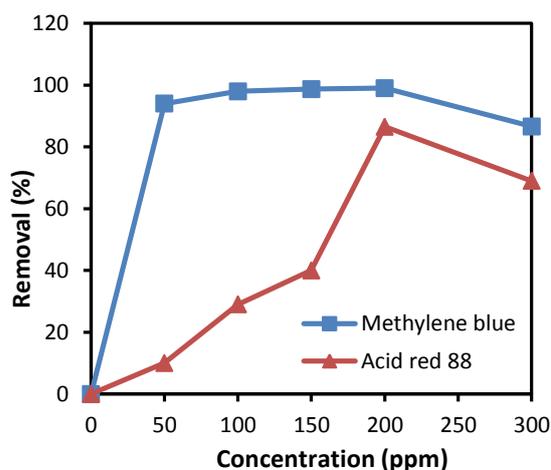


Figure 7. The effect of initial concentration on the biosorption of dyes (Dye concentration: 200 ppm, contact time: 60 minutes, biosorbent amount: 4 gram).

Biosorption for the same amount of grams for methylene blue is observed for all the concentrations at high removal percentages. Higher percentages of removal were obtained in the initial concentration of 200 ppm for acid red 88. When the other results of acid red 88 are examined, it is seen that this removal rate of the dye has also decreased after a rise. At this point, methylene blue also draws the same curve in a micro size. This is the cause of the parabolic curve, which first increases until its peak point and then decreases. This decrease can be explained by the insufficient pores of biosorbent due to the abundance of the dye concentration.

3.3. The effect of the amount of biosorbent on biosorption

To measure the effect of the amount of biosorbent on the removal of the dyes, the experimental conditions were selected as the dye solutions of 200 ppm, the interaction time of 60 min, the pH = 7, and room temperature. As can be seen in Figure 8, the increase in the amount of dyes per gram of biosorbent indicates that the remaining concentration decreases.

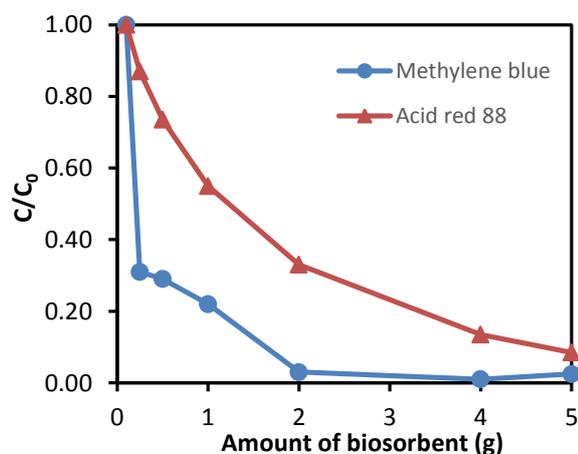


Figure 8. The effect of biosorbent amount of on the biosorption of dyes (Dye concentration: 200 ppm, contact time: 60 minutes).

According to the biosorption results of the two dyes, the increase in mass of biosorbent i generally leads to higher removal. When the test results for the methylene blue dye is examined, very similar removal rates are observed after a period of 1-2 grams. It can be understood that 1-2 grams of biosorbent can be used as the optimum amount of removal.

3.4. The effect of temperature change on biosorption

In order to measure the effect of temperature change on biosorption, the experimental results were obtained at pH 7, 200 ppm of dye concentrations, 120 minutes of

interaction time and 2 grams of biosorbent quantities. As can be seen from Figure 9, an increase in temperature slightly increases biosorption. Therefore, the energy consumption due to increased temperature does not encounter its cost. The slightly increased removal with additional temperature is not cost effective for the biosorption process. Hence, room temperature level has is the optimum because of the huge loss of energy for a slight increase in removal in higher temperatures.

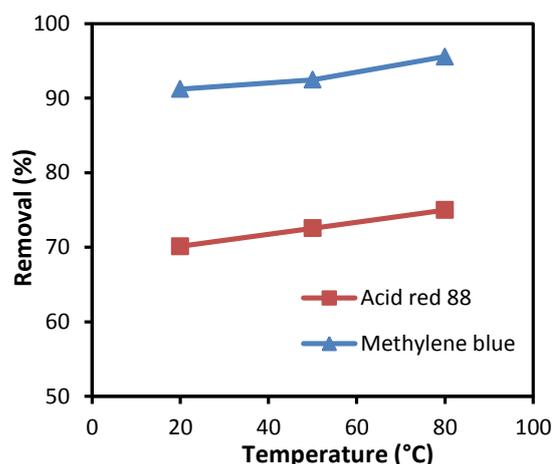


Figure 9. The effect of temperature on the biosorption of dyes (Dye concentration: 200 ppm, contact time: 120 minutes, biosorbent amount: 2 gram).

3.5. The effect of pH on biosorption

The effect of pH change on biosorption was carried out under the conditions initial dye concentration of 200 ppm, 120 minutes of interaction time and 2 grams of biosorbent. As can be seen in Figure 10, the best biosorption is obtained at pH 7. The same findings are also observed in the literature studies.²⁰

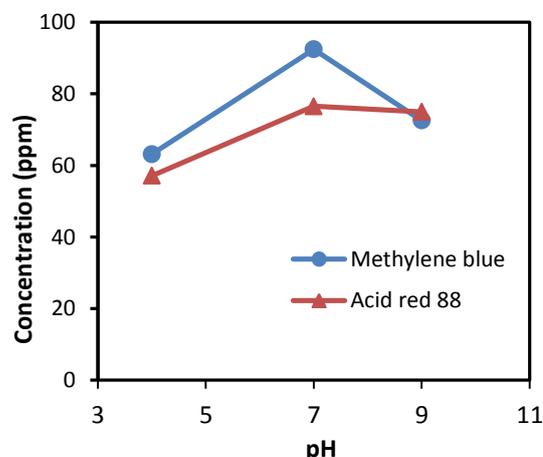


Figure 10. The effect of pH on the biosorption of dyes (Dye concentration: 200 ppm, contact time: 120 minutes, biosorbent amount: 2 gram).

All additional changes in pH level also affects the concentration of solution with the effect of H^+ or OH^- ions. Therefore, those additional hydronium or hydroxide ions can place into the empty pores of biosorbent instead of dye molecules. As can be seen in Figure 10, the optimum level of pH for biosorption is 7, indicating that no pH change is necessary to increase the removal of dye. Since the water is pure in its neutral pH range in the environment, it does not offer any additional action to achieve higher removal rates.

3.6. Biosorption isotherms

The biosorption isotherms of methylene blue and acid red 88 are studied according the Langmuir and Freundlich models in Equations (2) and (3), respectively. Isotherms were obtained for initial concentrations between 50 and 300 ppm for both dyes. The obtained isotherm parameters are given in Tables 1 and 2.

Table 1. Isotherm parameters of biosorption of methylene blue

Methylene blue			
	Langmuir		Freundlich
q_m	19.685	k	6.1854
K_L	0.5353	n	1.8761
R^2	0.8616	R^2	0.76

Table 2. Isotherm parameters of biosorption of acid red 88

Acid red 88			
	Langmuir		Freundlich
q_m	4.4091	k	0.1905
K_L	0.0181	n	1.6869
R^2	0.9898	R^2	0.9578

As can be seen from these Tables, Langmuir biosorption capacity (q_m) are found as 19.68 and 4.4091 $mg\ g^{-1}$ for methylene blue and acid red 88, respectively. The values of K_L which indicate biosorption energy were determined to be 0.5353 and 0.0181 $l\ g^{-1}$ for methylene blue and acid red 88, respectively.

The values of Freundlich biosorption capacity (k) isotherm are estimated as 6.1854 and 0.1905 $mg\ g^{-1}$ for methylene blue and for acid red 88, respectively. The values of n which indicate biosorption intensity were found as 1.8761 and 1.6869 $g\ l^{-1}$ for methylene blue and acid red 88, respectively. With the correlation coefficients of 0.86 and 0.9998 for methylene blue and acid red 88, the consistency to Langmuir isotherm was more good than Freundlich isotherm.

4. CONCLUSIONS

The wastewaters discharged to nature by the textile industry are rapidly becoming a globally increasing problem. These non-biodegradable dyes bring problems to the environment due to their toxic contents. For this reason, it is necessary to concentrate on the studies about the recovery of such wastes and toxic water. In this study, the removal of methylene blue and acid red 88 dyes that are used in the textile industry was investigated using peanut shell. In order to enlarge the surface area of the peanut shell, the pulverization process was made. The effects of biosorbent amount, contact time, initial dye concentration, pH, temperature, and type of dyes were investigated on the removal of the dyes by the biosorbent. At the result of the experiments, the highest removals for acid red 88 and methylene blue dyes were found as 88% and 99% under the experimental conditions studied, respectively. Biosorption isotherm followed best the Langmuir for both dyes. Because of the high removal rates obtained, the usage of peanut shell as an biosorbent can be a considerable alternative. These shells which can be easily obtained in most countries, are cheap and do not require industrial processing in any way, thus providing an alternative solution for the removal of contaminants from water. It is also possible that the peanut shell which are not subjected to any chemical treatment compared to activated carbon, can be supplied directly from the natural environment, and it can be used in an industrial context as a result of this work.

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Conflict of interest

Author states that there is no conflict of interest with any person, institute, company, etc.

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