Advances in Environmental Research, *Vol. 9, No. 2 (2020) 135-150*
DOI: https://doi.org/10.12989/aer.2020.9.2.135

Preparation of chitosan, sunflower and nano-iron based core shell and its use in dye removal

Esra Turgut*[1], Azize Alayli[1,2] and Hayrunnisa Nadaroglu[1,3]

[1]Faculty of Engineering, Department of Nano-Science and Nano-Engineering, Ataturk University, 25240, Erzurum, Turkey
[2]Department of Nursing, Faculty of Health Sciences, Sakarya University of Applied Sciences, 54187, Sakarya, Turkey
[3]Vocational School of Technical Sciences, Department of Food Technology, Ataturk University, 25240 Erzurum, Turkey

(Received December 27, 2019, Revised May 12, 2020, Accepted June 1, 2020)

Abstract. Many industries, such as textiles, chemical refineries, leather, plastics and paper, use different dyes in various process steps. At the same time, these industrial sectors are responsible for discharging contaminants that are harmful and toxic to humans and microorganisms by introducing synthetic dyes into wastewater. Of these dyes, methylene blue dye, which is classified as basic dyes, is accepted as a model dye. For this reason, methylene blue dye was selected in the study and its removal from the water was studied. In this study, two efficient biosorbents were developed from chitosan and sunflower waste, an agro-industrial waste and modified using iron nanoparticles. The biosorption efficiency was evaluated for methylene blue (MB) dye removal from aqueous solution under various parameters such as treating agent, solution pH, biosorbent dosage, contact time, initial dye concentration and temperature. We investigated the kinetic properties of dye removal from water for Chitosan-Sunflower (CS), Chitosan-Sunflower-Nanoiron (CSN). When the wavelength of MB dye was spectrophotometrically scanned, the maximum absorbance was determined as 660 nm. For the core shell biosorbents we obtained, we found that the optimum time for removal of MB from wastewater was 60 min. The pH of the best pH was determined as 5 in the studied pH. The most suitable temperature for the experiment was determined as 30℃. SEM-EDAX, TEM, XRD, and FTIR techniques were used to characterize biosorbents produced and modified in the experimental stage and to monitor the change of biosorbent after dye removal. The interactions of the paint with the surface used for removal were explained by these techniques. It was calculated that 80% of CS and 88% of CSN removed MB in optimum conditions. Also, the absorption of MB dye onto the surface was investigated by Langmiur and Frendlinch isotherms and it was determined from the results that the removal was more compatible with Langmiur isotherm.

Keywords: core shell; sunflower; chitosan; nanoiron; biosorbent; methylene blue

1. Introduction

The use of dyes is gradually increasing in the world and the need for dyes increases parallel to

*Corresponding author, Master Student, E-mail: esraturgut034@gmail.com

http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

time. Synthetic dyes are used in many industries such as pharmaceutical, food, cosmetics, plastics, leather and printing, as well as the textile industry (Aksoy 2012). In different areas of the industry, different dyes are used in various process steps (Ismail *et al.* 2013, Simonetti *et al.* 2016, Ahmad *et al.* 2015). The transfer of colored wastewater from these industries to natural streams causes many important problems, such as increasing the toxicity and chemical oxygen demand (COD) of wastewater and reducing light penetration, which has a negative impact on photosynthetic phenomena (Markovi *et al.* 2015). Artificial dyes used in said sectors have functional groups such as aromatic amines (azo dyes) and benzene ring in their chemical structure, which makes them carcinogenic (Simonetti *et al.* 2016). Therefore, the presence of these dyes in water, even in small quantities, causes a serious environmental problem. These dyes are chemically and phototically stable, and the complex aromatic structures of these dyes hinder the natural biodegradation process leading to turbidity as well as the odors of these wastewater (Ismail *et al.* 2013). So far, Dipa and Krishna have investigated the absorption and isotherms of methylene blue by using kaolinite, a type of clay (Dipa *et al.* 2002). Uddin *et al.* studied the absorptive removal of methylene blue dye using tea waste (Uddin *et al.* 2009).

Many authors have used herbal materials for absorption in their articles. Some of them are produced from the palm (Ahmed *et al.* 2011, Ahmed *et al.* 2012, Low *et al.* 2013). Chitosan-based absorbents have attracted considerable attention in the absorption of dyes. Chitosan is one of the world's most abundant and cost-effective biopolymers with various properties as an ideal absorbent for removing contaminants from wastewater. Initially, chitin is obtained by boiling in potassium hydroxide solution to produce an acid-soluble product called chitosan (Vakili *et al.* 2014).

Many researchers have investigated the adsorption performance of different chitosan forms. Chitosan from Chitin; A high crystallinity solid material called chitosan flakes was used by several researchers as an adsorbent for dye removal from aqueous solutions. Chitosan powder obtained from shrimp wastes was investigated by adsorption ability to remove different dyes from aqueous solution (Piccin *et al.* 2011). Cao *et al.* have used modified chitin. For this purpose, they obtained porous chitin using different chemicals and used this material for the removal of MB dye (Cao *et al.* 2018). After the introduction of hybrids in the 1980s, the yield of sunflower (*Helianthus annuus L.*) increased greatly. Anatomically, hybrid species include larger leaf areas, larger flower heads, increased plant height, and longer seeds. Increased plant biomass due to wider leaf area, higher plant height and shorter leaf stem, and therefore smaller plant diameters, will increase plants per hectare without reducing leaf area (Kaya 2016). However, this biomass that remains after harvest is a major problem for farmers. Therefore, it is an important research area that sunflower wastes can be used in different fields.

In our research, we aimed to develop a new core shell biosorbent using sunflower head waste and chitosan and to modify the biosorbent by coating nanoiron on this new biosorbent. Then, we used the nanobiosorbent obtained to remove MB dye from water. We investigated the effect of different components (pH, temperature, concentration, etc.) on the biosorbents which we obtained. We applied different techniques to see the superficial and molecular changes (UV-Vis, SEM-EDX, TEM, FTIR and XRD) after interactions of both the bio and nanobiosorbent we obtained with the dye. Using the data we obtained, we tried to find the most suitable model by drawing Freundlich and Langmuir isotherms equations for CS and CSN biosorbents.

2. Material method

2.1 Preparation of biosorbents

2.1.1 Supply of sunflower sample

The sunflower used in the studies was collected from the Botanical garden of Erzurum Atatürk University in September 2018 at the time of the dismantling of sunflowers. The seeds were separated from the collected sunflowers and the tray part was subjected to the washing process and then dried in daylight. The dried sunflowers were pulverized with the help of a blender. Powdered sunflower was stored in the 4^{o}C at non-moisture until was used.

2.1.2 Synthesis of iron nanoparticles

Synthesis of iron nanoparticles has been achieved by using 1 mM $FeCl_2$-$FeCl_3$ solution and fig (*ficus carica*) plant using a green synthesis method as Nadaroglu and the group previously did. (Gungor *et al*. 2015, Karaduman *et al*. 2017, Nadaroglu *et al*. 2017).

2.1.3 CS (Chitosan-Sunflower) core shell synthesis

CS (Chitosan-Sunflower) Core Shell was synthesized like previously described by Turgut (Turgut 2019).

2.1.4 CSN (Chitosan-Sunflower-Nano iron) core shell synthesis

After forming chitosan sunflower beads, modified with iron nanoparticles described by Nadaroğlu *et al*. and Turgut. (Turgut 2019, Nadaroglu *et al*. 2018).

2.2 Dye removal tests

2.2.1 Determination of optimum conditions for biosorption

In order to determine the most suitable conditions for determining the biosorption capacity of MB dyestuff; temperature, pH, amount of biosorbent and dye concentration stages were examined separately and optimum conditions were determined.

2.2.2 Spectrophotometer wavelength screening for dyes

At the end of the experimental studies, a 5 mL reaction mixture was taken from the solutions prepared to determine the most suitable conditions for dye biosorption. After centrifugation, the maximum peak wavelength of the MB dyestuff was determined with the Epoch ™ Microplate UV Vis Spectrophotometer. For wavelength scanning, the blind measurement was made by using pure water on the spectrophotometer and 3 mL of dye (50 mg/L) was added to the quartz cuvette. Wavelength scanning showed the wavelength at which the strongest peak was determined. In the experimental studies which were carried out at the optimal wavelength determined for the dyestuffs, measurements were made using the same wavelength value for the determination of dyestuff. In addition, calibration curve was prepared by measuring absorbance in samples with known dye concentration at a determined wavelength.

2.2.3 Determination of contact time

Samples were taken from the mixture at specific time intervals between 5 and 300 min. to determine the optimum contact time for MB stain removal. The dyes used were methylene blue, chitosan sunflower (CS) and chitosan sunflower nano iron (CSN) biosorbents at a concentration of 15 mL (25 mg/L) and 300 mg. At the end of contact time, prior to determining the concentration of MB by UV/Vis spectrophotometer the samples were centrifuged and filtered. Each adsorption experiment was conducted in triplicate and the average value was used in data analysis. The

adsorption amounts of MB onto nano-adsorbents (CS and CSN) were calculated according to the following Eq. (1):

$$q_e = \frac{(C_i - C_e)\, V}{\mathrm{M}} \tag{1}$$

2.2.4 Temperature effect

The effect of temperature on dyestuff biosorption process was investigated at 10 different temperatures (5-80^{o}C) for CS and CSN. As a result of the experimental study, the optimum temperature was determined for biorsorbent substances.

2.2.5 pH effect

The efficacy of bio sorbents was investigated in the range of 2-10 pH. The initial dyestuff concentration was 25 mg/L. The pH of the reaction medium of the dyes was adjusted to the desired values with 0.1M HCl/NaOH solutions, then 10 mL of the solutions were taken and 25 mg of biosorbent was added and mixed in the magnetic stirrer for the optimum time. The mixture was centrifuged at 6.000xg for 5 min. to separate the solid and the liquid. Absorbance measurements were performed in the liquid phase and the optimum pH was determined by spectroscopic method.

2.2.6 Determination of the amount of biosorbent

The effect of the amount of biosorbent on the biosorption capacity was investigated in the range of 6.25-100 mg biosorbent substance. Different amounts of biosorbents weighed on the analytical balance were added to 10 mL of dye solutions at a concentration of 25 mg and then mixed in the magnetic stirrer at the optimum contact time. Then, after 5 min. centrifugation at 6.000 rpm, the determination of the dyestuff from the liquid part was carried out spectrophotometrically.

2.2.7 Determination of dyestuff concentration

In order to determine the optimum dye concentration; A fixed amount of biosorbent material was used for MB dyestuff. Remediation study was performed by adding 25 mg of biosorbant substance to 10 mL dyestuff solutions in the range of 100-1.56 mg/L concentration. At the end of the experimental study, optimum dyestuff concentration was determined for MB remediation to be performed using CS and CSN.

2.3 Characterization of CS and CSN capsule

The resulting CS, CSN and CS-MB, CSN-MB were identified and identified using UV-VIS-NIR (Shimadzu UV-3600 Plus), SEM (Scanning Electron Microscope) (Zeiss brand), XRD (X-ray powder diffraction) (Panalytical Empyrean brand) and FT-IR (Fourier Transform Infrared) after the synthesizing, washing and drying steps.

2.4 Adsorption isotherms

The relationship between the amount of azo dye adsorbed by the amount of unit adsorbent at constant temperature and equilibrium solution concentration or pressure is known as ‘adsorption isotherm’. The amount of material to which the unit mass of the adsorbent material is adsorbed as

soon as the system reaches equilibrium during the adsorption process is a function of temperature, concentration, pressure or equilibrium pressure. In cases where the temperature is kept constant, this function is equal to the following equation;

2.4.1 Langmiur adsorption isotherm model

Langmiur isotherm is expressed by Eq. (2).

$$q_e = \frac{qo.\mathrm{KL}\,.\mathrm{Ce}}{1+Kl\,.Ce} \tag{2}$$

When the necessary corrections are made in this equation, the following equation is obtained.

2.4.2 Freundlich adsorption isotherm model

Freundlich isotherm Eq. (3);

$$q_e = K_f.\ C_e^{1/n} \tag{3}$$

Here;

Kf = Freundlich constant

n = It is constant. (n>1)

Taking the logarithm of the above equation, the following Eq. (4) is obtained;

$$\mathrm{nqe} = \ln Kf + \frac{1}{n}\ln Ce \tag{4}$$

2.4.3 Adsorption kinetics

The following Eq. (5) was used to determine the adsorption rate (Basibuyuk and Forster 1997).

First order Lagergren equation:

$$\log\frac{qe-q}{qe} = -\frac{k1,adt}{2.303} \tag{5}$$

Pseudo quadratic reaction rate Eq. (6);

$$\frac{t}{q}\left[\frac{1}{k2,adq2eq}\right] + \frac{1}{qeq}t \tag{6}$$

Quadratic speed Eq. (7);

$$\frac{1}{(qe-qt)} = \frac{1}{qe} + kt \tag{7}$$

$K_{1,ad}$ = Lagergren adsorption rate constant (min^{-1})

$K_{2,ad}$= pseudo quadratic adsorption rate constant (g/mg.min)

k = quadratic adsorption rate constant (g/mg.min)

qe=Amount of substance adsorbed when equilibrium occurs (mg/g)

qt= Amount of adsorbed substance at any given time (mg/g)

The log (qe-qt), t/qt and 1/(qe-qt) values were plotted against t value and $K_{1,ad}$, $K_{2,ad}$ and k values were calculated.

2.4.4 Adsorption thermodynamics

In adsorption, the entropy decreases as the adsorbent becomes more regular with accumulation.

Adsorption to be spontaneous (spontaneous) in the following Eq. (8) ΔH^o value must be negative (exothermic) (Nollet *et al.* 2003).

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (8)$$

ΔG^o= Free energy exchange (kJ/mol)
ΔH^o= Enthalpy change (kJ/mol)
ΔS^o= Entropy change (kJ/mol K)
T = Absolute temperature (Kelvin)
R = Gas constant (8,314 J/mol K)
kc= Equilibrium constant

Eq. (9) was used to find the Gibss free energy of adsorption at a given temperature;

$$K_c = \frac{Ca}{Ce} \quad (9)$$

K_c= Equilibrium constant
Ca = Amount of substance retained in the mass of the adsorbent (mg/g)
Ce = Concentration of substance remaining in solution (mg/g)

The Gibs free energy of adsorption was found by placing Kc in the equation (10) below with the help of the above equation (Dakikiy *et al.* 2002).

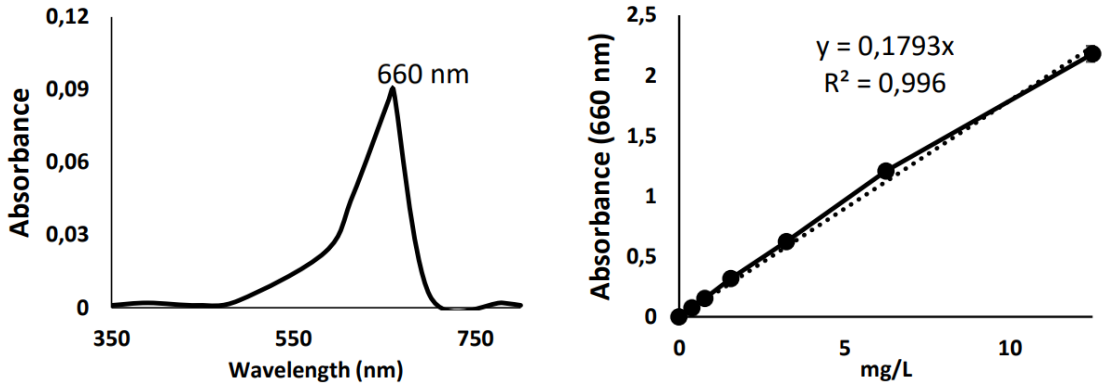
$$\Delta G^o = -RT\ln K_c \quad (10)$$

Using the last Eq. (11) below, the slope ΔH^o and the intersection ΔS^o of the $\ln_{Kc}$ value plotted against 1/T (Van't Hoff) were calculated (Nollet *et al.* 2003).

$$\ln K_c = \frac{\Delta So - \Delta Ho}{R} x \frac{1}{T} \quad (11)$$

3. Results and discussion

For the standard solution prepared at a concentration of 5 mg/L, wavelength scanning was performed using a UV-Vis spectrophotometer.



(a) (b)

Fig. 1 (a) Wavelength scan of methylene blue dye at a concentration of 5 mg/L and (b) Standard chart for methylene blue dye at a concentration range of 0.39-12.5 mg/L

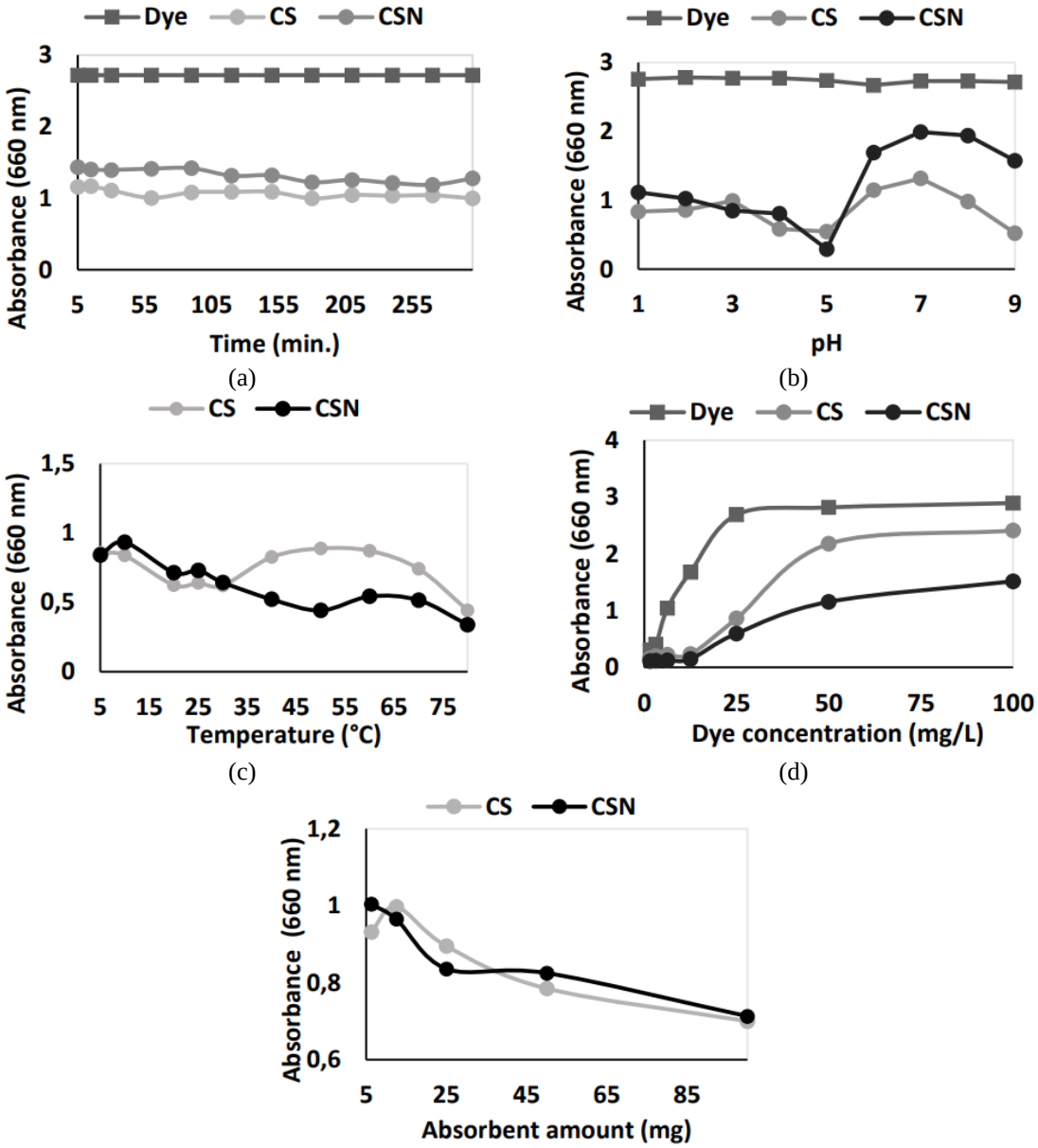


Fig. 2 Determination of the interaction time (a), pH (b), temperature (c), dye concentration (d) and adsorbent amount (e) for CS and CSN for methylene blue dye

For MB staining, Beckman Coulter brand UV-Vis spectrophotometer was used for screening, the highest sharp peak at 660 nm was determined and the results are given in Fig. 1(a). Uddin *et al.* showed that MB gave the highest peak at 664 nm in their dye wavelength scan and supports our result (Uddin *et al.* 2009).

Absorbance measurements were made for MB dye at a concentration of 0.39-12.5 mg/L at 660 nm and it was found that linear standard graph can be drawn from the obtained values (Fig. 1(b)).

Other measurements were made to be diluted to these ranges. The formula (12) obtained from the graph was used to calculate the amount of MB retained by the solution and/or absorbent.

$$x = \frac{y}{0{,}1793} \tag{12}$$

In the given graph, MB dye was removed from the solution in proportion to time as a result of interaction with absorbant. As can be seen from the graph above, it is understood that a large part of the absorption is completed within 60 min. (Fig. 2(a)). The biosorbent synthesized by its modification with nano iron was provided to increase the surface area, become more charged and become easily reused by creating a magnetic field from the reaction medium. It is obtained by synthesizing with cheap method and cost is reduced. In this way, the cost of the process also decreases (Nadaroglu *et al.* 2015). Uddin *et al.* determined the duration of dye absorption procedure as 6 hours by using tea waste (Uddin *et al.* 2009). Cao *et al.* Adsorbent material with porous surface containing different concentrations of chitin (0.9%-3.5%) was prepared and characterized using FT-IR, XRD and SEM chromatographic methods. It was determined from the experimental results that the adsorbent had a low crystal structure and a high porous surface. It was determined that the adsorbent containing the chitin content prepared and characterized removes methylene blue dye by 79.8% (Cao *et al.* 2018).

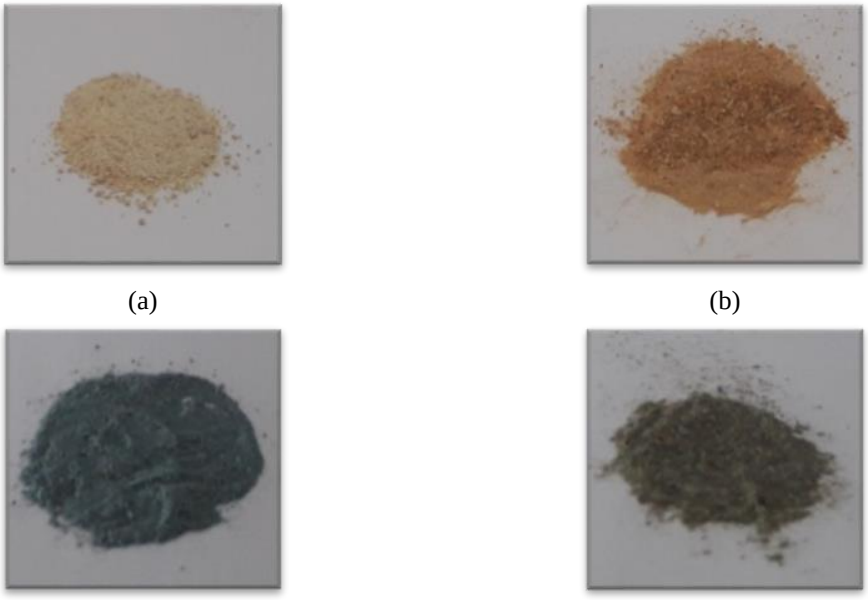
The biosorption of the dyestuffs was examined at a pH of 2-10. The initial dyestuff concentration was 25 mg/L. 10 mL aliquots of the solutions whose pH was adjusted to the desired values were taken and 25 mg of biosorbent was added and mixed in the magnetic stirrer for the specified time. The mixture was centrifuged at 6000 xg for 5 min. to separate the solid and the liquid. Dyes were determined by UV spectroscopic method in liquid phase. The optimal pH value for the dyestuffs was determined for MB: pH 5.0 (Fig. 2(b)).

In the biosorption studied on tea wastes, pH was found to be 8 by Uddin *et al.* They have determined the optimum pH range as 5-10 for methylene blue dye (Uddin *et al.* 2009). Salimi *et al.* indicated that the optimum conditions for were pH = 9 and 5 g L^{-1} Cu-goethite as well as pH of 10 and 7 g L^{-1} goethite along with the contact time of 30 min (Salimi *et al.* 2019).

In order to determine the effect of temperature on paint removal, removal of MB with CS and CSN adsorbents at different temperatures was measured using spectrophotometer at 660 nm, calculated according to Eq. (1) and the results are shown in Fig. 2(c). The optimum temperature for MB dye removal was found to be 30 ± 2℃ (Dipa *et al.* 2002). Uddin *et al.* determined the optimum temperature as 27 ± 2°C (Uddin *et al.* 2009).

As a result of the experimental study, the amount of biosorbant material was determined as 25 mg/mL MB for 10 mL dyestuff solution (Fig. 2(d)). In order to find the optimal amount of absorbant, varying proportions of absorbants were used and the obtained data were graphed in Fig. 2(e).

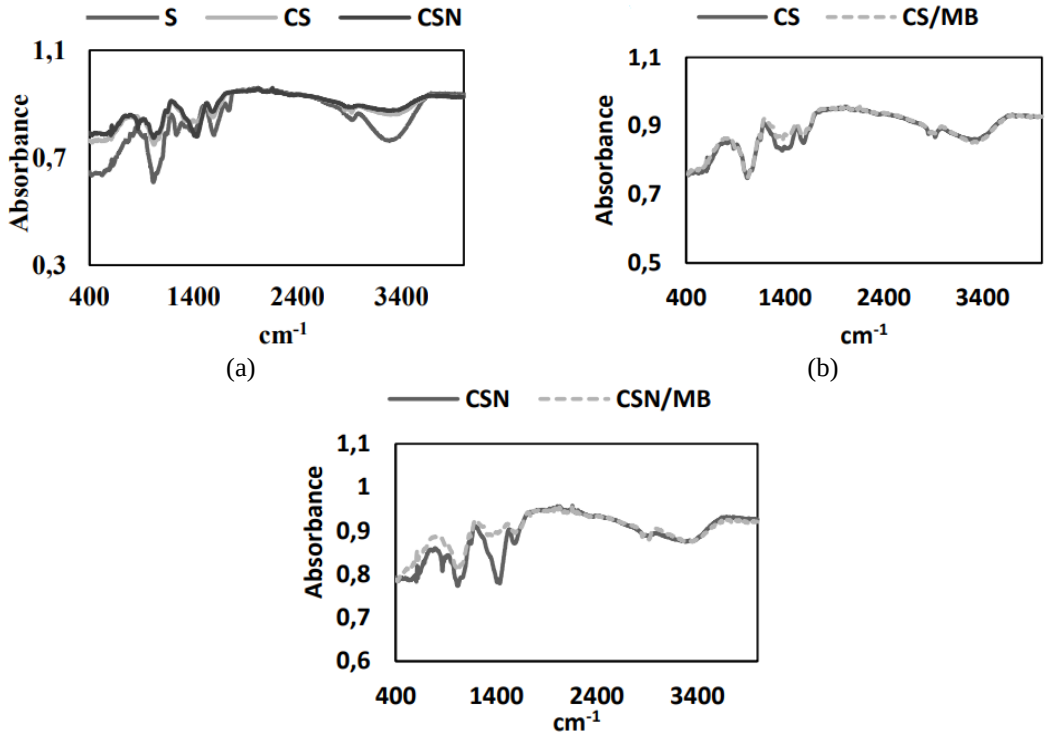
In a different study, optimum conditions using chitosan were determined at pH 3, 150 rpm, and acid blue 9 for 60 minutes and pH 3, 50 rpm. In these conditions, the adsorption capacities were reported to be 210 mg/g and 295 mg/g (Saha *et al.* 2010). Another group found that the highest adsorption capacity using chitosan was 9.95 mg/g at pH 4.0 and 3.86 mg/g at pH 9 (Mahmoodi *et al.* 2011, Dotto and Pinto 2011). In different research using Chitosan, the removal of Acid Blue 9 and Food Yellow 3 from waste water was investigated. The results showed that the capacity of chitosan powder for Acid Blue 9 and Food Yellow 3 was 50% and 60% respectively. In another study, the removal of Reactive Black M-2R (RBM) from waste water was also tested by using chitosan (Fang and Ding 2011). Chitosan was produced using both shrimp and Labeorohita and it



(a) (b)

(c) (d)

Fig. 3 CS (a) CSN (b) and CS-MB (c), CSN-MB and (d) image before dye removal of bio and nanobiosorbent materials



(a) (b)

(c)

Fig. 4 FT-IR graphs of S, CS, CSN (a), CS and CS-MB (b), CSN and CSN-MB (c)

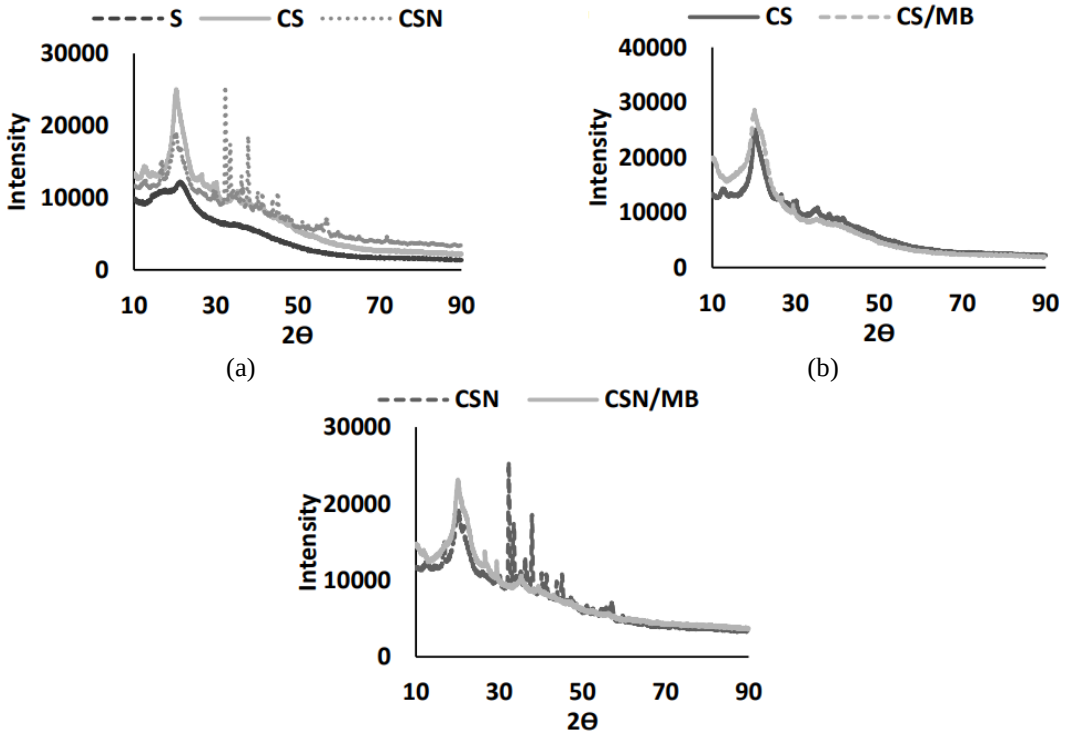


Fig. 5 XRD graphs of S, CS, CSN (a), CS, CS-MB (b) and CSN-MB(c)

was concluded that the dye was better removed at low pH (3 to 4) when the acid Yellow 73 adsorption capacity was studied (Iqbal *et al.* 2011, Rafatullah *et al.* 2009).

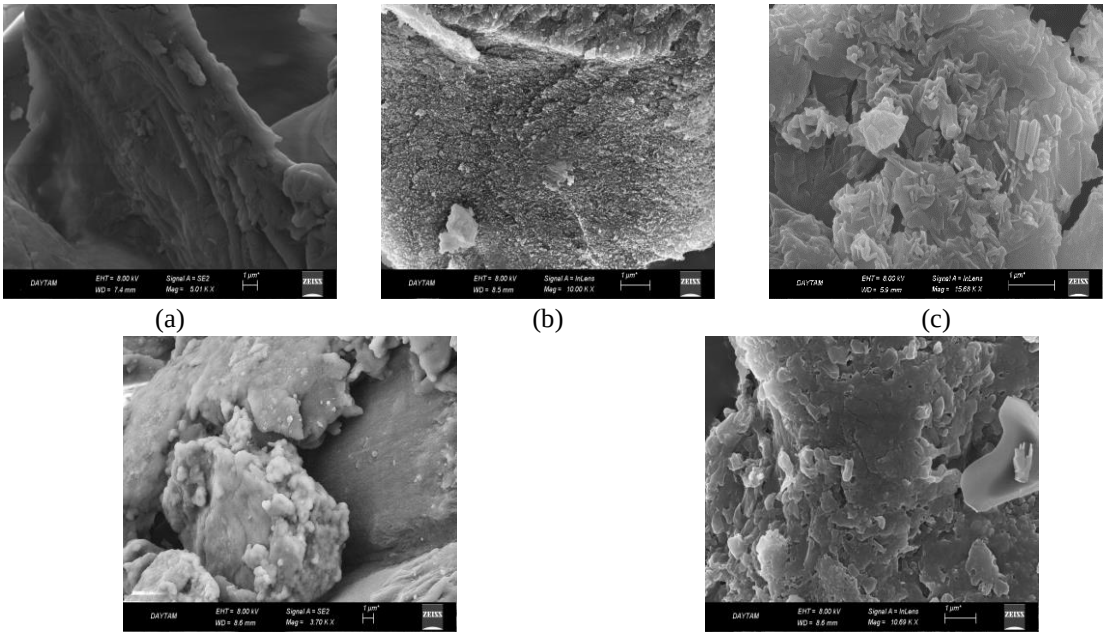
In our research, it was understood that the reaction medium provides the best removal in 30ºC at room temperature close to the neutral environment such as pH 5 in a short time such as 60 minutes. When the necessary calculations were made under these environmental conditions, it was determined that 80% of CS and 88% of CSN removed the dye from water.

During the characterization processes, the biosorbents were dried and photographed before and after adsorption and are shown below in Fig. 3.

The FTIR spectra of CS (a) and CSN (b) before and after MB adsorption are shown in Fig. 4.

The function groups on sunflower tray waste as shown in Fig. 4(a), and the spectra display a number of absorption peaks, indicating the complex nature of sun-flower tray waste. The interactions of sunflower waste and chitosan are also shown in Fig. 4. Subsequent changes in the functional groups in CSN synthesized by coating with iron nanoparticles are shown in Figure 4a. FTIR spectra of MB-loaded CS and CSN showed that the peaks expected at 3214, 2966, 1662 and 1456, 1070 cm^{-1} had shifted, respectively, to 3429, 2966, 1656, 1431 and 1068 cm^{-1} due to MB adsorption. The shift in peak position represents the contribution of that functional group in the adsorption process (carboxyl, hydroxyl and amine). Minor changes observed in other frequencies were not considerable (Fig. 4(b) and 4(c)).

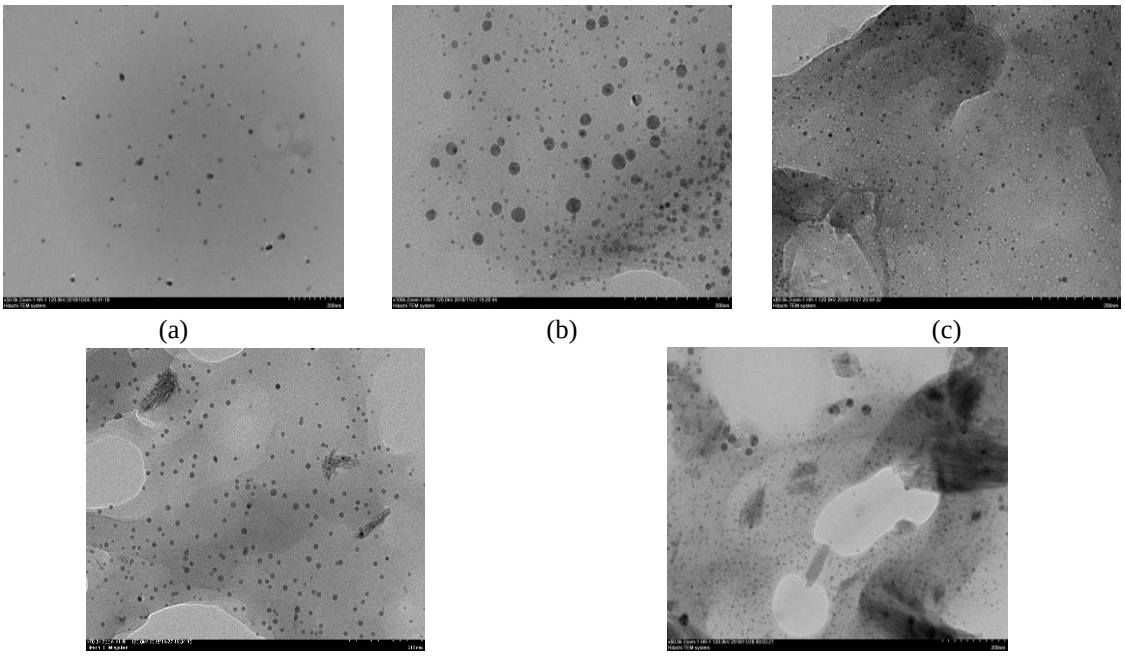
XRD peaks at 19.20º, 27.49º, 32.43º gives the CS structure peaks while the structure of the NPs connected to the peaks of the CS structure in addition to 32.28º, 32.17º and 37.82º in the presence of peaks of Fe NPs were determined.



(a) (b) (c)

(d) (e)

Fig. 6 SEM imagines of S, CS, CSN (a, b and c), CS, CS-MB (d) and CSN-MB (e)



(a) (b) (c)

(d) (e)

Fig. 7 TEM imagines of S, CS, CSN (a, b and c), CS, CS-MB (d) and CSN-MB

When MB, CS and CSN adsorbed on the 19.78^{o}, 24.24^{o}, 27.15^{o}, 32.73^{o} and 36.97^{o} peaks and

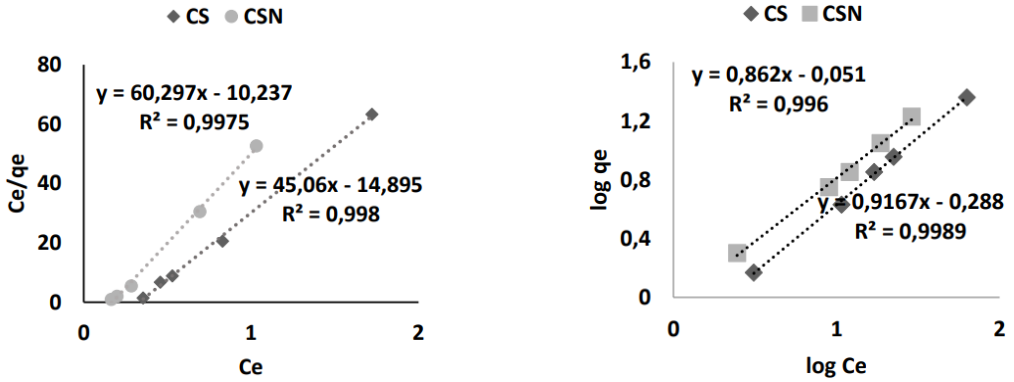


Fig. 8 Adsorption isotherms for the adsorption of MB onto CS and CSN. The inserts: the values of lnQ_e against lnC_e based on the Freundlich isotherm model and the linear dependence of C_e/Q_e on C_e based on the Langmuir isotherm model

after the paint adsorption showed that all peaks show a little shift in Fig. 5(a)-5(c).

SEM images of CS and CSN adsorbents before and after MB stain removal are given in Fig. 6 and TEM images in Fig. 7. When SEM analysis is examined, it is seen that Fe_3O_4 NPs bound to CS structure are around 6-20 nm. It shows a homogeneous distribution on the CS surface, but in some parts of the structure, clusters and aggregations appear due to its magnetic structure. Therefore, particle diameters grow and particles reaching 60 nm are outstanding. It was found that both CS and CSN removal of MB dye was performed successfully under optimum conditions (time; 60 min. PH; 5 and temperature; 30°C). It is clear from both SEM and TEM analysis that the surface of CS and CSN is coated with MB dye. However, it is determined from Figs. 6 and 7 that the MB dye of CS coated with Fe_3O_4 NPs is more effective.

The 1/T graph of Ln_{KL} obtained from biosorption of methylene blue dyes with CS and CSN biosorbent substances is given in the following figures. Adsorption kinetics of MB dye and CS and CSN biosorbent substances and MB dye at concentrations of 12.5, 25 and 50 mg/L were investigated in dyestuff solutions. In order to determine the adsorption constants, firstly the suitability to the first order reaction kinetics was examined. For this purpose, firstly ln (qe-qt) is plotted against time. R_2 values were also calculated for 12.5, 25 and 50 mg/L concentrations and these values are given on the graph. Langmuir and Freundlich isotherm graphs of CS and CSN biosorbent materials used in the experimental study were drawn for the biosorption of methylene blue dye by using Langmuir isotherm equation. Langmuir isotherm equation used in the study is given below (13). The correlation between Ce/qe and Ce calculated from the experimental results of Langmuir isotherm is given in the following Fig. 8.

$$\frac{Ce}{qe} = \frac{1}{kVm} + \frac{Ce}{Vm} \tag{13}$$

The equation used in Freundlich isotherm calculations is given below (14). The correlation between Log_{qe} and Log_{Ce} calculated from experimental results is given in the following figures.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{14}$$

The inserts: the values of lnQ_e against lnC_e based on the Freundlich isotherm model and the linear dependence of C_e/Q_e on C_e based on the Langmuir isotherm model.

Table 1 Values of the Langmuir and the Freundlich adsorption isotherm models

Langmuir Adsorption Model			**Freundlich Adsorption Model**		
Langmuir constants	**CS**	**CSN**	**Freundlich constants**	**CS**	**CSN**
Q_{max}	52.25	61,34	K_F	0.102	0.183
K_L	0.674	0,745	b_F	0.68	0.797
R^2	0.998	0,997	R^2	0.996	0.998

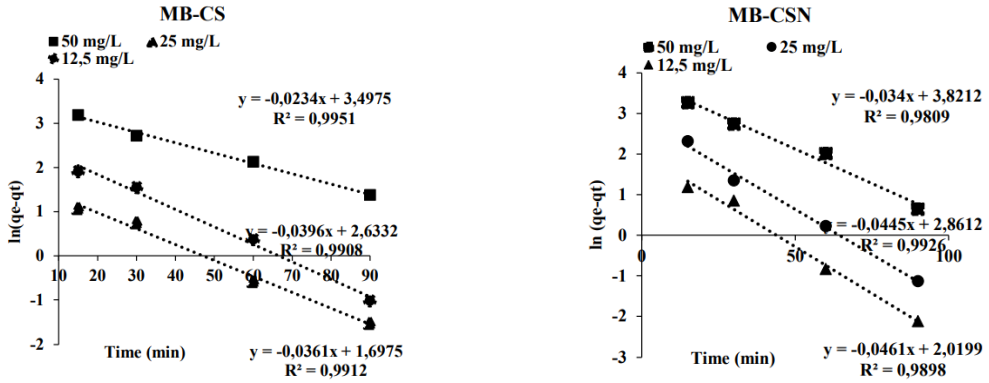


Fig. 9 Pseudo-first-order reaction for MB adsorbed onto CS and CSN at different concentrations

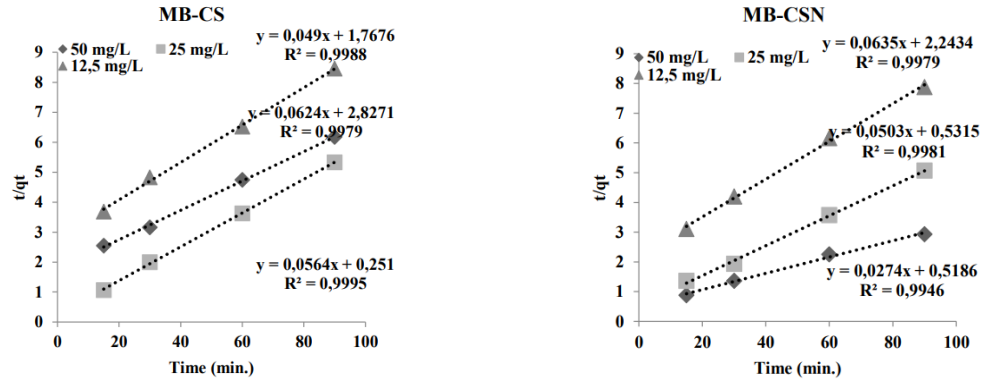


Fig. 10 Pseudo-second-order reaction for MB adsorbed onto CS and CSN at different concentrations

The values of Q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e from Fig. 8 and the Langmuir parameters were presented in Table 1. The isotherm was found to be linear entire concentration range studied with good linear correlation coefficients (R^2= 0.998 and 0.987) for CS and CSN, showing that data correctly fit the Langmuir model in both cases.

Similarly, the value of lnQ_e against lnC_e according to the experimental isotherm data was shown in the inset of Fig. 8. The calculated values of Freundlich parameters were illustrated in Table 1. The corresponding R^2 for adsorption of MB onto CS and CSN adsorbents were 0.996 and 0.998, respectively. Compared with the Freundlich isotherm model, the Langmuir isotherm model better represents the equilibrium adsorption of MB onto CS and CSN, suggesting that the adsorption process is the monolayer coverage of the dye on the surface of CS and CSN adsorbent.

Table 2 Kinetic parameters for the adsorption of MB onto CS and CSN

		Pseudo-first-order rate equation			Pseudo-second-order rate equation		
Initial MB concentration (mg/L)	**Q_e-exp (mg/g)**	**k_1**	**Q_e-cal (mg/g)**	**R^2**	**k_2**	**Q_e-cal (mg/g)**	**R^2**
CS absorbent							
5	8.64	0.0571	1.042	0.995	18.10^{-3}	11.65	0.998
25	14.2	0.0333	18.11	0.991	$14.5.10^{-3}$	19.26	0.999
50	35.6	0.0328	24.45	0.990	$21.74.10^{-3}$	48.46	0.997
CSN absorbent							
5	8.81	0.0547	0.689	0.980	$11.47.10^{-3}$	11.74	0.994
25	16.72	0.0416	16.21	0.992	$7.93.10^{-3}$	19.8	0.998
50	38.25	0.287	24.22	0.989	$5.18.10^{-3}$	43.19	0.997

In similarly, for the pseudo-second-order models, linear plots of t/Qt against t give high R^2 values range from 0.997 to 0.999 and from 0.994 to 0.998 for CS and CSN adsorbents (Figs. 9 and 10, Table 2), respectively. The very high correlation coefficients suggest that the pseudo-second-order model is a suitable model for dye removal by CS and CSN adsorbents, respectively.

Compared with for the pseudo-first-order model, the pseudo-second-order model is closer to unity and the calculated Qe values computed from pseudo-second-order equation show very good agreement with experimental values. This indicates that the pseudo-second-order kinetic model is more applicable for the adsorption of MB onto CS and CSN adsorbents.

4. Conclusions

Although chitosan biosorbent has been studied as a biosorbent by a large number of groups, it has been determined that biosorbent capacity is limited. During this study, sunflower waste and chitosan were used as low-cost natural biosorbents for the removal of MB dye from aqueous solutions. Biosorption productivity was tested by using different biosorption conditions. The biosorbent surface on chitosan was increased by using sunflower waste. In addition, better results have been obtained by using different biosorption materials. Iron nanoparticles, on the other hand, increased the effect of adsorption more due to its interaction with paint. The CS and CSN biosorbents we produce have been found to be more efficient than most absorption processes. The conditions of obtaining and the ease of synthesis add a very advantageous to the use of these two biosorbents. The conditions of obtaining and the ease of synthesis add a very advantageous to the use of these two biosorbents. The reason for CSN to remove more MB from the water than CS is that the nano iron in the structure of CNS is due to the enzyme mimic properties. For this reason, it is thought that synthesized biosorbents can find a wide range of applications with cheap and eco-friendly character that can be used repeatedly.

References

Ahmad, A., Mohd-Setapar, S.H., Chuong, C.S., Khatoon, A., Wani W.A., Kumar, R. and Rafatullah., M.

(2015), "Recent advances in new generation dye removal technologies: Novel search for approaches to reprocess wastewater", *RSC Adv*., **5**(39), 30801-30818. https://doi.org 10.1039/C4RA16959J.

Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., Nasir, M. and Ibrahim, M. (2012), "The use of date palm as a potential adsorbent for wastewater treatment: A review", *Environ. Sci. Pollut. Res*., **19**(5), 1464-1484. https://doi.org 10.1007/s11356-011-0709-8.

Ahmad, T., Rafatullah, M., Ghazali, A., Sulaiman, O. and Hashim, R. (2011), "Oil palm biomass-based adsorbents for the removal of water pollutants-a review", *J. Environ. Sci. Health Part C*, **29**(3), 177-222. https://doi.org 10.1080/10590501.2011.601847.

Aksoy, O. (2012), "Evaluation of pomegranate paste as a new adsorptor for removal of some dyestuffs and copper metal from the aqueous solution", Master Thesis, Dicle University, Diyarbakir, Turkey.

Basıbuyuk, M. and Forster, C.F. (1997), "An examination of the treatability of a simulated textile wastewater containing maxilon red", *Process Biochem*., **32**(6), 523-527. https://doi.org/10.1016/S0032-9592(97)00007-1.

Cao, Y.L., Pan, Z.H., Shi, Q.X. and Yu, J.Y. (2018), "Modification of chitin with high adsorption capacity for methylene blue removal", *Int. J. Biol. Macromolecul*., **114**, 392-399. https://doi.org/10.1016/j.ijbiomac.2018.03.138 .

Dakikiy, M., Khamıs, M., Manassra, A. and Mer'eb, M. (2002), "Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents", *Adv. Environ. Res*., **6**(4), 533-540. https://doi.org/10.1016/S1093-0191(01)00079-X.

Dipa, G. and Bhattacharyya, K.G. (2002), "Adsorption of methylene blue on kaolinite", *Appl. Clay Sci*., **20**(6), 295-300. https://doi.org/10.1016/S0169-1317 01)00081-3.

Dotto, G.L. and Pinto, L.A.A. (2011), "Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism", *J. Hazard. Mater*., **187**, 164-170. https://doi.org/10.1016/j.jhazmat.2011.01.016.

Fang, L. and Ding, C. (2011), "Adsorption of reactive black m-2r on different deacetylation degree chitosan", *J. Eng. Fibers Fabrics*, **6**(3), 155892501100600303. https://doi.org/10.1177/155892501100600303.

Gungor, A.A., Celebi, N. and Nadaroglu H. (2015), "Removal of basic red 9 in wastewater using green fenton reaction", *Fresenius Environ. Bull*., **24**(5B), 1947-1957.

Iqbal, J., Wattoo, F.H., Muhammad, H.S., Malik, R., Tirmizi, S.A., Imran, M. and Ghangro, A.B. (2010), "Adsorption of acid yellow dye on flakes of chitosan prepared from fishery wastes", *Arab. J. Chem*., **4**(4), 389-395. https://doi.org/10.1016/J.Arabjc.2010.07.007.

Ismail, B., Hussain, S.T. and Akram, S. (2013), "Adsorption of methylene blue onto spinel magnesium aluminate nanoparticles: adsorption isotherms, kinetic and thermodynamic studies", *Chem. Eng. J*., **219**, 395-402. https://doi.org/10.1016/j.cej.2013.01.034.

Karaduman, I., Gungor, A.A., Nadaroglu, H., Altundas, A. and Acar S. (2017), "Green synthesis of y-fe_2o_3 nanoparticles for methane gas sensing", *J. Mater. Sci. Mater. Electron*., **28**(21), 16094-16105. https://doi.org/10.1007/s10854-017-7510-5.

Kaya, Y. (2016), *Sunflower*, in *Breeding Oilseed Crops for Sustainable Production*, Academic Press, 55-88.

Low, L.W., Teng, T.T., Rafatullah, M., Morad, N. and Azahari, B. (2013), "Adsorption studies of methylene blue and malachite green from aqueous solutions by pre-treated lignocellulosic materials", *Sep. Sci. Technol*., **48**(11), 1688-1698. https://doi.org/10.1080/01496395.2012.756912.

Mahmoodi, N.M., Salehi, R., Arami, M. and Bahrami, H. (2011), "Dye removal from colored textile wastewater using chitosan in binary systems", *Desalination*, **267**, 64-72. https://doi.org/10.1016/j.desal.2010.09.007.

Markovi, S., Stankovi, A., Lopicic, Z., Lazarevi, S., Stojanovi, M. and Uskokovi, D. (2015), "Application of raw peach shell particles for removal of methylene blue", *J. Environ. Chem. Eng*., **3**(2), 716-724. https://doi.org/10.1016/j.jece.2015.04.002.

Nadaroglu H., Gungor A.A. and Celebi N. (2015), "Removal of basic red 9 (BR9) in aqueous solution by using silica with nano-magnetite by enzymatic with fenton process", *Int. J. Environ. Res*., **9**(3), 991-1000. https://doi.org 10.22059/IJER.2015.987.

Nadaroglu, H., Alaylı Güngör, A. and Ince, S. (2017). "Synthesis of nanoparticles by green synthesis method", *Int. J. Innov. Res. Rev.*, **1**(1), 6-9.

Nadaroglu, H., Lesani, A., Soleimani, S.S., Babagil, A. and Güngör, A.A. (2018), "Efficient solar photocatalyst based on TiO_2 /corn silk NPs composite for removal of a textile azo-dye from aqueous solution", *IIOAB J.*, **9**(4), 20-27.

Nollet, H., Roels, M., Lutgen, P., An Der Meeren, P. and Verstraete, W. (2003), "Removal of pcbs from wastewater using fly ash", *Chemosphere*, **53**, 655-665. https://doi.org/10.1016/S0045-6535(03)00517-4.

Piccin, J.S., Dotto, G.L. and Pinto, L.A.A. (2011), "Adsorption isotherms and thermochemical data of fd&c red no 40 binding by chitosan", *Braz. J. Chem. Eng.*, **28**(2), 295-304. https://doi.org/10.1590/S0104-66322011000200014.

Rafatullah, M., Sulaiman, O., Hashim, R. and Ahmad, A. (2009), "Adsorption of methylene blue on low-cost adsorbents: A review", *J. Hazard. Mater.*, **177**(1-3), 70-80. https://doi.org 10.1016/J.Jhazmat.2009.12.047.

Saha, T.K., Bhoumik, N.C., Karmaker, S., Ahmed, M.G., Ichikawa, H. and Fukumori, Y. (2010), "Adsorption of methyl orange onto chitosan from aqueous solution", *J. Water Resour. Protect.*, **2**, 898-906. https://doi.org 10.4236/jwarp.2010.210107.

Salimi, F., Rahimi, H. and Karami, C. (2019), "Removal of methylene blue from water solution by modified nanogoethite by Cu", *Desalination Water Treatment*, **137**, 334-344. https://doi.org 10.5004/dwt.2019.22922.

Simonetti, E.A.N., Cividanes, L.D.S., Campos, T.M.B., Menezes, B.R.C.D., Brito, F.S. and Thim, G.P. (2016), "Carbon and TiO_2 synergistic effect on methylene blue adsorption", *Mater. Chem. Phys.*, **177**, 330-338. https://doi.org /10.1016/j.matchemphys.2016.04.035.

Sulfath, T.S., Bhanu, K.M., Koneru, V., Aparna, R.M. and Ann, V.K. (2019), "Case report on methylene blue induced hemolytic anemia", *Int. J. Med. Res. Health Sci.*, **8**(5), 83-85.

Turgut, E. (2019), "Chitosan, nanoparticle and sunflower plant based biosorbent material production and investigation of usability for dye removal", Master Thesis, Atatürk University Nanoscience and Nano Engineering, Erzurum, Turkey.

Uddin, M.T., Islam, M.A., Mahmud, S. and Rukanuzzaman M. (2009), "Adsorptive removal of methylene blue by tea waste", *J. Hazard. Mater.*, **164**(1), 53-60. https://doi.org 10.1016/j.jhazmat.2008.07.131.

Vakili, M., Mohd, R., Babak, S., Ahmad, Z.A., Mahamad, H.I., Kok, B.T., Zahra, G. and Parisa, A. (2014), "Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review", *Carbohyd. Polym.*, **13**, 115-130. https://doi.org 10.1016/j.carbpol.2014.07.007.

CC