Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
Turgut & al. / Mor. J. Chem. 9 N°3 (2021) 564-575

Synthesis of Nano-biocomposite Adsorbent and Investigation of Remediation of Reactive Black 5 Dye from Wastewater

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Received 10 0ct 2020,
Revised 03 Sept 2021,
Accepted 19 Nov 2021

Abstract

When the wastes generated as a result of industrial production are directly released to the environment, they cause pollution of the ecosystem, which is valuable for all living things, with harmful and toxic substances and their derivatives. One of the most important of these wastes is synthetic chemical dyes. A lot of work is being done on waste management and waste disposal due to its importance. The purpose of our work was developed a new non-toxic and biodegradable biosorbent using sunflower waste material and chitosan. Later, we modified these biosorbents with nano-iron molecules to investigate the usability of this bio and nano-biosorbent in the removal of Reactive Black 5 (RB5) dye. The optimum removal conditions for RB5 dye were determined by examining the parameters (pH, temperature, contact time, etc.) for the removal of Reactive Black 5 dye. Surface and molecular changed and kinetic characterizations for bio and nano-biosorbent before and after dye removal were examined by UV-vis, SEM, TEM, FT-IR and XRD techniques. For UV-vis analysis, 597 nm was used as the highest absorbance wavelength of RB5. In paint removal studies using CS and CSN, the optimum dye removal time was found to be 90 minutes. For CS and CSN, it was determined that the optimum temperature 40 and 50 ºC and acidic pH (2-4) were higher for RB5 dye removal, respectively. The superficial and molecular changes of the synthesized nano-biosorbent after its interactions with the dye have been demonstrated and explained using different techniques. It is understood from the results that it can adsorb 22.5 mg / g dye for CSN and 21.59 mg/g for CS. These removal rates and the fact that we have obtained these rates using bioabsorbent shows that the method can be used to successfully remove RB5 dye.

Keywords: *Reactive Black 5, Nano biosorbent, Dye removal, Sunflower waste, Bio-synthesis*

1. Introduction

Production in textile industries is directly dependent on water. Therefore, the waste water of these industries contains high amounts of dyes. Almost half of the dyes used in textiles are azo dyes, a significant amount of dyes used in other industries such as printing, toy and pharmaceutical production [1,2]. Approximately, 15% of the dyes used in this industry are discharged to the environment as waste [3,4]. There are 5 main methods for cleaning water containing waste dyes. These are adsorption, oxidation (ozonation etc.), biological remediation, coagulation-precipitation and membrane use [5] Adsorption process is more advantageous than other methods because it is simple, economical and easy to apply. In addition, the adsorption method can be applied in the removal of concentrated dyes [6]. Adsorption technique is preferred among the techniques mentioned because of its easy, inexpensive, and successful and biomaterial use feature. Although activated carbon is the most preferred of these adsorbents, other biosorbents are needed due to its losses in regeneration and its cost. Therefore, finding easily accessible, cheap and environmentally friendly adsorbents is an important research area. Some of these adsorbents have been used in many materials such as sawdust, palm kernel fibber, activated carbon produced from pea shell and broad bean, plant roots and shellfish [7]. One of the researches in this field is about the use of sunflower seed pods. It was used as a low cost and effective adsorbent to remove RB5, a diazo dyestuff, from water. In addition, Osma et al. used tangerine peels as biosorbents and conducted a potential study on dye removal capacity of RB5 removal [7].

A different study describes the removal of RB5 dye from the dye solution using the biomass of two brown algae, *Macrocystis pyrifera* and *Undaria pinnatifida* [8]. Chitosan is one of the other most promising bio-sorbents for adsorption. Their use for adsorption of many molecules (dyes, metals, ions, phenols, pharmaceuticals, pesticides and herbicides etc.) has been investigated. Chitosan (CS) based membranes have unique advantages such as abundance of resources, good biocompatibility, having sufficient areas (amino and hydroxy) for adsorption of heavy metals and organic pollutants, making them a promising material. As a result, CS-based membrane types have been developed for different biosorbents [9]. It has also been used for azo-dye removal by modifying chitin. In different studies conducted in this way, a biosorbent with different properties has been developed. Auta and Hameed prepared a chitosan and clay composition for both batch and fixed bed adsorption experiments. It has been studied by another research group that prepared a magnetic nanocomposite of chitosan/β-cyclodextrin for methylene blue removal [10,11]. Elwakeel et al. prepared a resin based on chitosan and glutaraldehyde and using it, they removed the cationic dye BRR250 from wastewater [12]. The removal of reactive red dye was performed by using an adsorbent produced from chitosan and graphene oxide molecules modified with chitosan [13]. Gao and his group; they chose an anionic dye (AR18) to investigate the adsorption properties of chitosan functionalized with siliceous mesopause SBA-15 [14]. Another anionic dye, RB 19, was removed from wastewater using chitosan graphene and poly (methyl methacrylate) [15, 16]. RB5 is a tetra sulfonated diazo dye. It is widely used in the textile industry to dye cellulose and cotton fibres [17]. With the disposal of RB5 to the environment, the respiratory system of the creatures exposed to paint can be damaged. It can cause acute bronchitis, skin irritations, mutations and major ailments such as bladder cancer. For the reasons listed, it is very important to clean the RB5-containing wastewater before discharging it to the environment. In a research conducted; banana peel powder, waste tea leaves, pumpkin seed shells and egg shells have been used as a biosorbent to remove RB5 from water [18,19]. Nanotechnology has been used in all fields at full speed. Nanoparticles; it has unique optical, electrical and thermal properties. Nanoparticles have an indispensable role in many fields such as medicine, diagnosis, imaging, detection, genetics, artificial implants and tissue engineering [20]. In

addition, nanoparticles are used in environmental protection and waste water treatment. Green synthesis methods developed for the synthesis of non-toxic nanoparticles are an important and reliable method in terms of nanobiotechnological researches [21, 22]. In the study, a new biosorbent substance was synthesized by green synthesis using sunflower plant waste and chitosan. This biosorbent material has been modified using iron nanoparticles obtained by biosynthesis. Bio and nanobiocomposites synthesized afterwards were used to remove RB5 dye from water in order to improve waste water. Kinetic data related to the adsorption and thermodynamics obtained are discussed.

1. Materials and methods

Sunflower used for green synthesis of biosorbent substances in the studies was collected from Ataturk University hobby gardens in Erzurum in September 2019. The fig (Ficus caricas) plant required for the green synthesis of iron nanoparticles added to biosorbent substances was collected from Sakarya province in June-August, 2019. The chemicals used in the study were Chitosan (Sigma/Aldrich 75% purity), Acetic acid (CH3COOH - Sigma/Aldrich 100%), Sodium hydroxide (NaOH-Merck 99-100%), Hydrochloric acid (Merck-HCl 37%), Hydrogen peroxide (H2O2; 35%). The dyes used for dye solutions in the experimental stage are Reactive Black 5 (Sigman/Aldrich≥50%), Iron (III) chloride (FeCl3; Sigma/Aldrich 97%) and Sodium phosphate (Na3PO4; Merck≥99%).

1.1. Nanosorbent and nanobiosorbent preparation

The sunflower waste material was first washed and cleaned using tap water then distilled water and then dried and pulverized. In the experiment, sunflower powder and chitosan were used by mixing at a ratio of 1:1. The prepared mixture was polymerized in 100 mL of 5% acetic acid (CH3COOH). Biosorbent beads were formed by dropping polymerized chitosan sunflower mixture into 2 M sodium hydroxide (NaOH) solution with the aid of a syringe (CS). After the bead formation, iron-oxide (Fe3O4) nanoparticles obtained by the method of Nadaroglu et al. were added to the base solution to bind iron to the beads. The interaction of the positive charges on the iron nanoparticles with the negative charges on the chitosan surface has made it possible to coat the nano iron particles on the biosorbent surface. The material obtained after filtering and washing processes was dried in the oven at 40 oC for 1 night and then turned into powder. In this way, chitosan sunflower iron oxide (CSN) nanobiosorbent material was obtained [22-25].

1.2. Characterization of nanosorbent and nanobiosorbent

The subsequent CS, CSN and CS-RB5, CSN-RB5 were recognized 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).

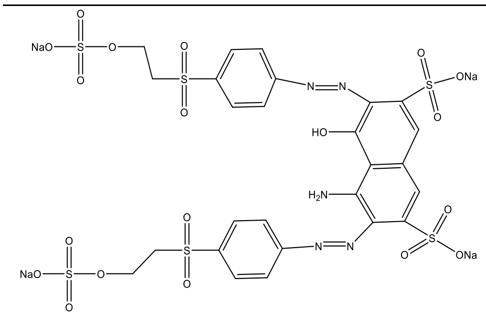
1.3. Investigation of the kinetics of RB5 dye removal

The relationship between the amount of azo dye adsorbed by the unit amount of adsorbent at constant temperature and the equilibrium solution concentration or pressure is known as the "adsorption isotherm". As a result of our experiments, when the system came to equilibrium, calculations were made using equations and data.

2. Results and Conclusion

The chemical structure and properties of Reactive Black 5 (RB5) are given in table 1. Colour changes of the adsorbent before and after the adsorption process using synthesized CS and CSN are shown in figure 1.

Table 1. Chemical structure and properties of Reactive Black 5 (RB5)

Name	Synonym	Molecular Formula	Molecular weight	Security Alert
	Reactive Black 5, Remazol Black B	$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.82	May cause respiratory sensitization, mutagenic, carcinogenic and organ toxicity[17].

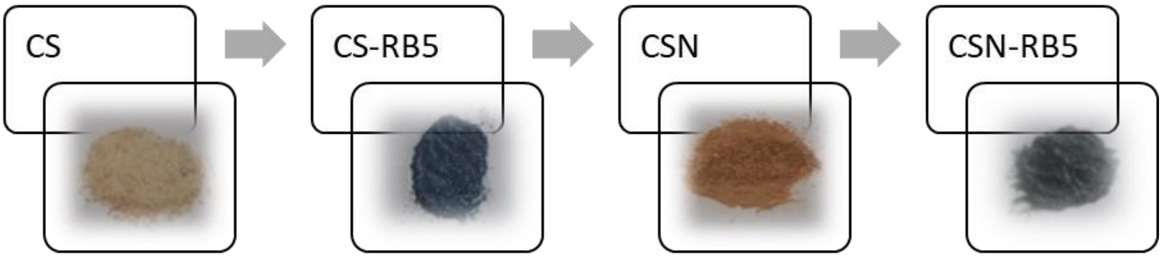


Figure 1. Color changing of CS and CSN with RB5

2.1 Determination of optimum pH, temperature and concentrations for paint removal

When the wavelength of the RB5 dye is scanned, the maximum absorbance wavelength was determined as 597 nm (Figure 2).

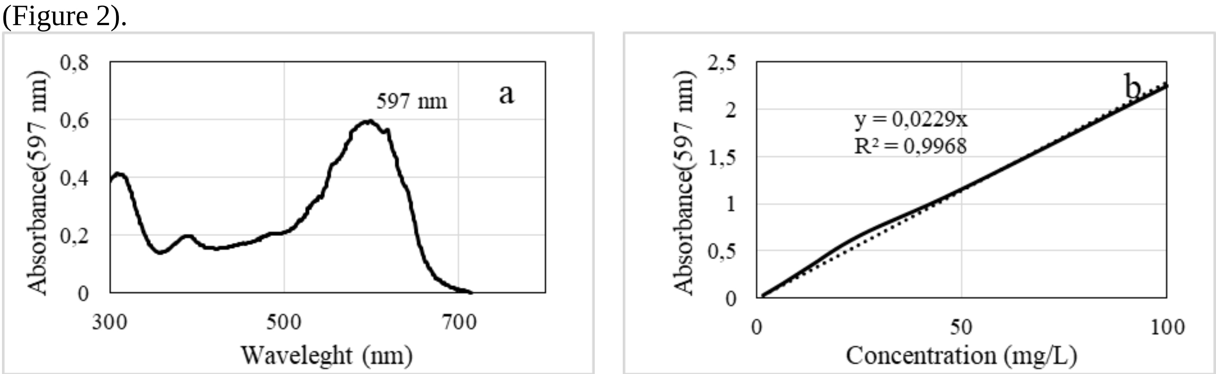


Figure 2. Wavelength scanning spectrum of RB5 dye (a) calibration graph for RB5 azo dye (b)

In order to determine the wavelength at which the RB5 dye gives maximum absorbance, the wavelength scanning for the standard solution prepared using pure water at a concentration of 50 mg/L was performed using UV-Vis spectrophotometer and it was observed that it gave the highest absorbance at 597 nm (Figure 2a). The concentration versus absorbance plot for the RB dye was found to be linear between 1.56-100 mg/L and other measurements were made by diluting these ranges. The formula (I) obtained from the graph was used to calculate the amount of RB that is lost from the solution and / or retained by the absorbent (Figure 2b).

$$x = \frac{y}{0,0229} \qquad \text{(I)}$$

In another study in which sunflower seed hulls and RB 5 dye were removed, as a result of the experiments performed with UV-Vis spectrophotometer, 597 nm, which is the same value as we found, as the wavelength at which the dye gives maximum absorption. And this absorbance parameter was used in kinetic studies. (Figure 2A) [7].

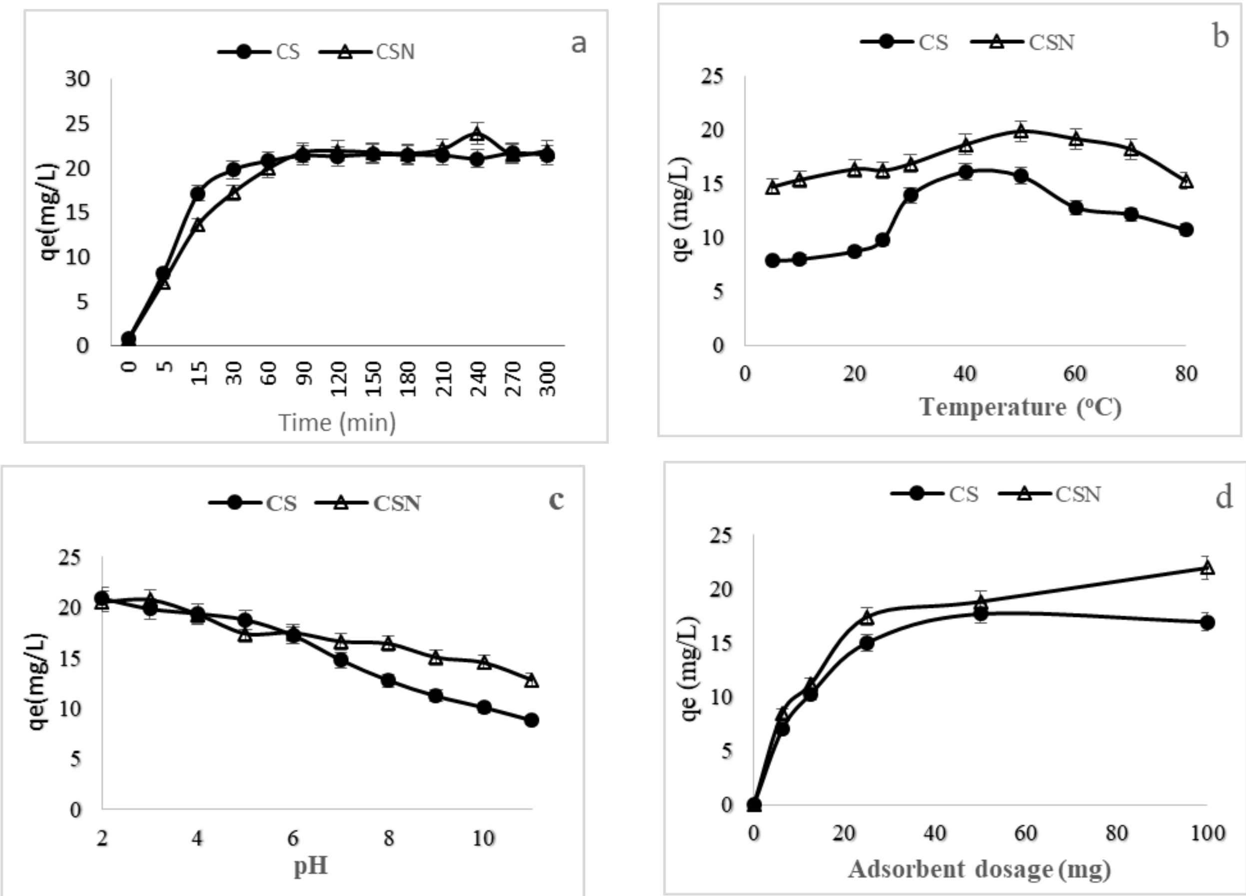


Figure 3. Effect of contact time (**a**), temperature (**b**), pH (**c**) and adsorbent dosage (**d**) on RB5 dye adsorption by CS and CS (initial RB5 concentration: 25 mg/L, adsorbent dose: 25 mg/25 mL, stirring speed: 400 rpm).

In the graph given for RB5, as a result of the interaction of the dye with the adsorbent, the removal from the solution in proportion to the time was observed. It was observed that equilibrium adsorption was reached in the removal of RB5 in approximately 90 min. (Figure 3a). In the study with sunflower seeds and mandarin peels, the optimum time was determined as 210 min. [7]. In a study using two different algae species, the maximum adsorbing capacity was reached in the 400 minute. The effect of temperature on dye removal for RB5 was determined as 50 ºC for CS and CSN measured using RB dye at different temperatures (Figure 3b). Similarly, Muatanga et al., in their study using macadamia seed, stated that the optimum adsorption temperature was as 60 ºC [19]. The effect of pH on dye removal for RB5 was measured. It was determined that the most suitable pHs were in the range of 2-3 which are acidic pHs (Figure 3c). In their experiments using macadamia seed Husks, Muatanga et al. stated that the optimum pH was 3 [19]. In a different study using potato peel wastes, it was shown that the optimum pH for RB5 dye removal was 3 [26]. In a study using sunflower seed pods and mandarin peels, it was shown that the optimum pH for RB5 dye removal was 2. In the study using chitosan, it was observed that the maximum absorption capacity was reached when the pH of the environment was lowered [27]. In a study conducted with two different algae, algae biomass were used and it was stated that the optimum pH was 1. In addition, high pH is used for desorption of the dye [8]. It is understood from figure 3c that our experimental findings for optimum pH are compatible with the data in the literature. In Figure 3d, experiments were made using variable amounts of adsorbents with constant dye concentration and it was seen that it could adsorb the amount of dye that increased with the increase of the adsorbent. It is understood from the experimental results that CSN can adsorb 22.5 mg/g and CS 21.59 mg/g dye. *M. pyrifera* biomass (26.31 mg/g) and *U. pinnatifida* biomass (12.64 mg/g) reported as the maximum adsorption capacity [8]. The absorption capacity for

chitosan flakes was found to be 39.5 mg/g, 91.25 mg/L for sun flower seed peel and 2.5 g/50 mL for mandarin peel. In a study using different algae, 99% dye removal was reported [8]. Dye removal was shown to be 85.5% in a study using potato peel waste [26]. It was reported that sunflower husk and mandarin peel wastes were removed the dye from waste water by the rate of 85% and 71%, respectively [7]. Dye removal percentages were studied with synthesized adsorbents and RB5 removal was found to be 90.04% and 86.35% for CSN and CS, respectively.

2.2. Characterization

UV-Vis spectrophotometer, SEM-EDX, TEM, XRD and FT-IR techniques were used for the characterization of the bio/nanobiosorbent material. Afterwards, the mentioned techniques were used to monitor the dye removal experimentally (Figures 4.5.6 and 7).

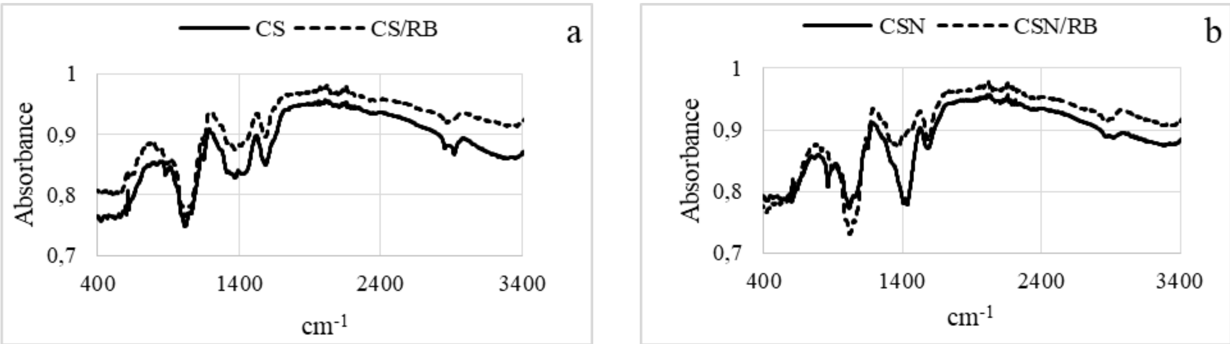


Figure 4. FT-IR spectrums of RB5 and bio and nano biosorbent interaction

FTIR spectrum of RB5 dye interacting with CS and CS is given in Figure 4a, while the spectrum of RB5 dye interacting with CSN and CSN is given in Figure 4b. While the formation of peaks between 1000-1700 cm^{-1} originating from iron in the spectrum of CSN were compared to CS, it was observed that the size of the peaks decreased on the surface covered with RB5 [28].

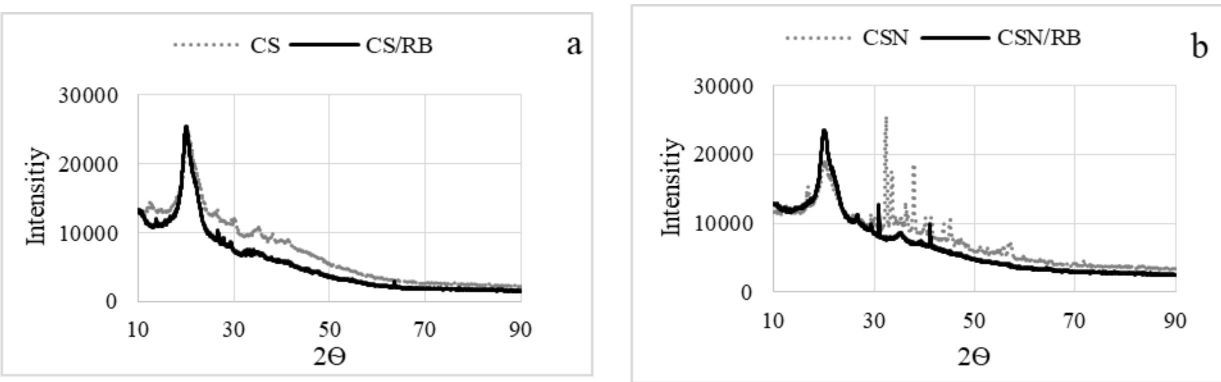


Figure 5. XRD spectrums of RB5 and bio and nano biosorbent interaction

While the XRD spectrum of the RB5 dye absorbed on CS and CS was seen in Figure 5a, Figure 5b showed the XRD spectrum of the RB5 dye absorbed on CSN and CSN. When looking at CS and CSN, XRD peaks originating from nano iron could be understood from the figure. In addition, when the paint is attached to the CSN surface, it was understood that the intensity of the nano iron peaks decreased. In Figure (6a, b, c and d), the surface changes in CS and CSN bio and nanobiosorbents are clearly seen from the SEM images. It is understood from the shapes that the

paint covers the surface and creates a less porous structure. Figure 7 shows the TEM spectra of CS and CSN both before and after RB5 absorption. In the image obtained, it was understood from the way that the nanostructures grow by clustering after the dye is treated.

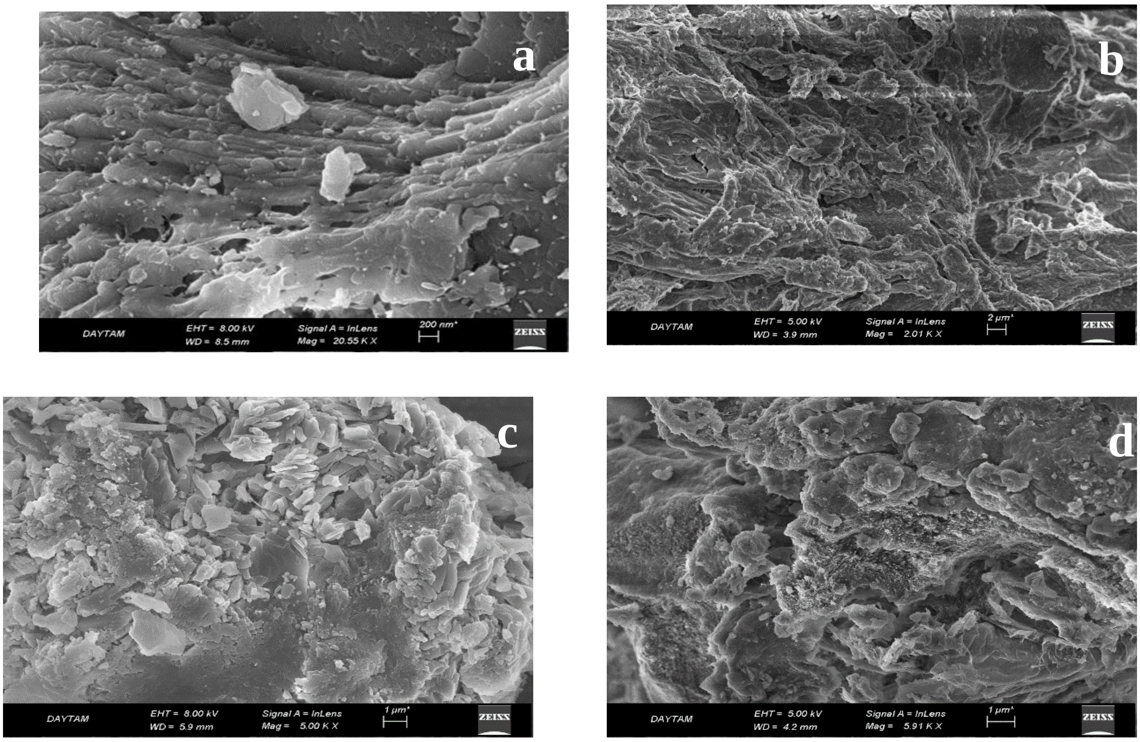


Figure 6. SEM images of bio and nanobiosorbent (a: CS, b: CS- RB5, c: CSN and d: CSN-RB5)

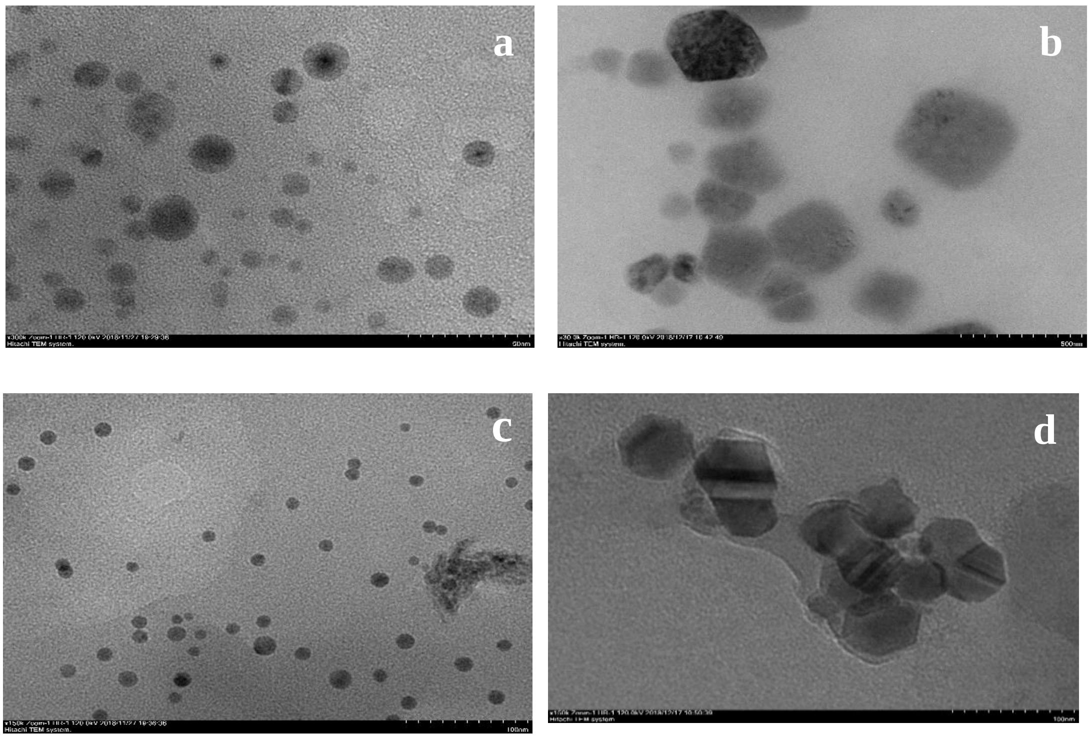


Figure 7. TEM images as a result of interaction of CS and CSN with RB5 (a: CS, b: CS-RB5, c: CSN, d: CSN-RB5)

2.3. Adsorption Isotherms

2.3.1. Langmuir Adsorption Isotherm

Using the Langmuir isotherm equation, Langmuir isotherm graphs of the biosorption of RB5 substances of CS and CSN biosorbent materials used in the experimental study were drawn. The equation used in the study was given below (II). The relationship between Ce/qe and Ce calculated from the experimental results was given in the figures 8 a, b and table 2 below.

$$\frac{Ce}{qe} = \frac{1}{kVm} + \frac{Ce}{Vm} \quad \text{(II)}$$

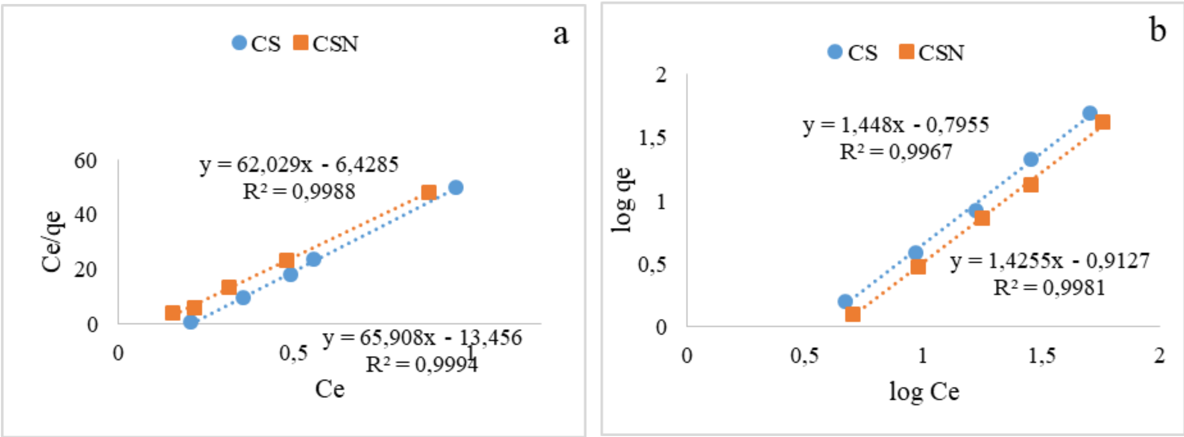


Figure 8. Langmuir isotherms (a) Freundlich isotherms (b) for biosorbent and biosorption of RB5.

2.3.2. Freundlich adsorption isotherm

By using Freundlich isotherm equation, isotherm plots of the adsorption of the RB5 dye of bio and nanobiosorbent compounds were drawn. The equation used in the study is given below. The relationship between $Logq_e$ and $LogC_e$ calculated from experimental results is given in the Figures 9 a,b and Table 2 below.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \text{(III)}$$

Table 2. Langmuir and the Freundlich constants for the adsorption isotherms.

Langmuir adsorption model			**Freundlich adsorption model**		
Langmuir constants	**CS**	**CSN**	**Freundlich constants**	**CS**	**CSN**
q_{max} *(mg/g)*	0.0152	0.016	K_F *(mg/g)*	0.451	0.369
b (L/mg)	4.89	97.08	*N*	0.702	0.691
R^2	0.999	0.998	R^2	0.997	0.998

2.4. Adsorption Kinetics

2.4.1. First and second order reaction kinetics

Adsorption kinetics of CS and CSN adsorbents and RB 5 dye at concentrations of 12.5, 25 and 50 mg/L were investigated in dye solutions. In order to determine the adsorption constants, first-order reaction kinetics were examined. For this, graphs of ln (qe-qt) against time are drawn first. In addition, R2 values were calculated for concentrations of 12.5, 25 and 50 mg / L. Qe and k1 values are calculated from the graphs obtained and given in Table 3.

$$\ln (qe-qt) = \ln qe - k_1 t \quad \text{(IV)}$$

Then, in order to calculate the adsorption constant of the same dye, its compatibility with the second order reaction kinetics was investigated. For this, the (t/qt) value was plotted against time. R^2 values were calculated for the dye concentrations of 12.5, 25 and 50 mg / L. In addition, the k2 constant was calculated using the reaction equation (IV). All values calculated for Reactive Black 5 were given in the table. (Table 3).

Table 3. Comparison of experimental and calculated qe values of first and second order adsorption rate constants in dye removal.

Reactive Black 5								
			First degree			**Second degree**		
Adsorbent Type	Initial Dye Concentration (mg/L)	qe, experimental (mg/g)	k1 (t/min.)	qe, calculated (mg/g)	R^2	k2 (g/mg.min.)	qe, calculated (mg/g)	R^2
CS	12.5	8.64	0.0471	0.379	0.989	$19.47.10^{-3}$	16.84	0.992
	25	14.2	0.0324	0.795	0.999	$15.52.10^{-3}$	20.7	0.989
	50	35.6	0.0316	1.218	0.995	$12.18.10^{-3}$	46.15	0.996
CSN	12.5	11.56	0.0527	0.294	0.997	$10.17.10^{-3}$	11.74	0.990
	25	22.49	0.0427	0.856	0.992	$6.79.10^{-3}$	24.16	0.984
	50	46.65	0.0286	1.327	0.989	$4.86.10^{-3}$	48.72	0.999

2.4.3. Calculation of Thermodynamic Parameters

The 1/T graph against LnKL obtained from the biosorption of RB 5 dye with CS and CSN biosorbent substances was given in the Figures 9.

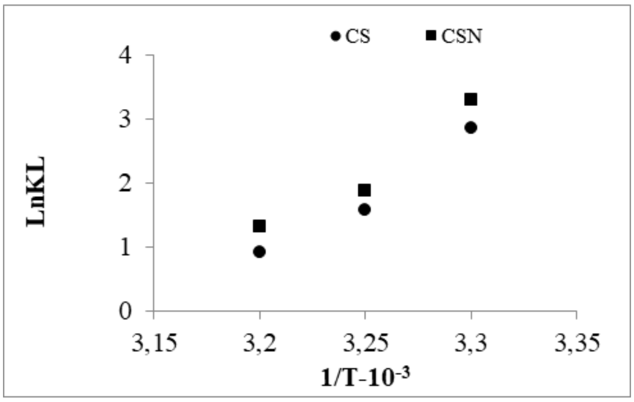


Figure 9. Thermodynamic kinetics plots of biosorption for CS and CSN adsorbents

When the ΔG ° values are calculated for the adsorption of RB5, the positive values obtained in the temperature range (293 K, 298 K and 303 K) indicate that the adsorption is not spontaneous. The resulting positive ΔG ° value indicates that adsorption requires external energy to convert reactants into products (Deniz 2010). The negative values of ΔH° more confirm the exothermic nature of the adsorption, and the negative ΔS° values indicate the increase in the adsorbate concentration in the solid-liquid (Table 4). It also confirms the increased randomness at the solid-liquid

interface during adsorption. This is the normal result of the physical adsorption process that takes place through electrostatic interactions [29,30].

Table 4. Thermodynamic constants for the biosorption of dyes using biosorbent materials

	RB5		
	ΔG° (kJ/mol.K)	**ΔH° (kJ/mol)**	**ΔS° (kJ/mol)**
CS 20 °C	150.94		
CS 25 °C	153.52	-160.79	-507.79
CS 30 °C	153.099		
CSN 20 °C	158.62		
CSN 25 °C	161.16	-164.20	-515.71
CSN 30 °C	163.69		

In the research carried out, it was observed that CS and CSN nanocomposites synthesized using chitosan and sunflower waste were highly removed RB5 dye from water by adsorption. As a result of the research findings, it was understood that CSN nanobiosorbent produced using environmentally friendly methods can be used effectively to remove RB5 dye from waste water. In addition, it has been seen as a result of the literature reviews that this method developed for dye expense yields better results than many studies used today. It is clear from the results of the studies that synthesized CS and CSN can be used either alone or in combination with other methods in the dye removing.

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