O 82. A NOVEL COMPOSITE BY COATING ACORN SHELL (QUERCUS VULCANICA) WITH CHITOSAN FOR REMOVAL OF CR (VI) FROM AQUEOUS SOLUTION

Şerife Parlayıcı[1], Elif Özdemir[2], Kübra Tuna[1], Erol Pehlivan[1]

[1]*Konya Technical University, Department of Chemical Engineering, Campus, 42079 Konya, Turkey*
[2]*Department of Chemical Engineering, Selcuk University, Campus, 42079 Konya, Turkey*

E-mail: serife842@hotmail.com, ozdmrelif1248@gmail.com, kubratnaa@gmail.com, erolpehlivan@gmail.com

ABSTRACT: Water contamination raised with rapid and irregular industrialization growing, so elimination of Cr (VI) ions from contaminated water before discharge is vitally important. The purpose of this study; using acorn shell (AS) and Chitosan-coated acorn shell (Cts◉AS) as a biomaterial in the removal of Cr (VI) from aqueous solutions. Cts◉AS composite was prepared by adding glutaraldehyde as a cross-linking agent and operational feasibility of Cts◉AS for Cr (VI) biosorption from aqueous environment was investigated by using different kinds of factors. The effects of contact time, initial solution pH, initial Cr (VI) concentration, and biosorbent amount on the elimination of Cr (VI) for AS and Cts◉AS composite were investigated by batch experiments. The biosorption system was tested using various isotherm models. The optimum conditions for the removal of Cr (VI) were found to be the amount of biosorbent 0.1 g, pH 2.0 and equilibrium time of 120 min for AS. On the other hand, the optimal conditions for the biosorption of Cr (VI) by Cts◉AS were found to be: 2.0-2.1 initial pH, 90 min of exposure duration, 0.05 g biosorbent amount, 150 mg/L of initial Cr (VI) concentration at 25 ℃. The maximum biosorption capacity calculated from the Langmiur was found to be 89.29 mg/g and 44.25 mg/g for Cts◉AS and AS, respectively. The characterization of Cts◉AS and AS were performed using two techniques; Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR). The produced a novel Cts◉AS composite is offering an alternative biosorbent for Cr(VI) removal from aqueous mediums.

Keywords: Biosorption, Composite, Chitosan, Acorn Shell, Cr (VI)

1. INTRODUCTION

The increases in industrial activities are caused to accumulate different kinds of environmental pollutants, which are one of the most significant results of environmental contamination and damage to the natural ecosystem (Ghasemi et al. 2015). Hazardous chemicals contact with soil and groundwater resources and cause serious problems for the human health and the environment (Banerjee, 2017). Especially, industrial wastewaters include heavy metals, which are seen as hazardous contaminants. Many heavy metals show toxic properties even if they are found in low concentrations in industrial wastewater. They are not biologically degraded in aqueous solutions, thus they accumulate in the body via the food chain and damage them. When toxic substances are released into water sources, mass fish deaths arise most of time in lake, sea, and rivers.

Chromium is very toxic heavy metal, which can be taken in different ways such as inhaled in the air, drift into drinking water and with the food chain. In addition, it can also be absorbed from the skin to a limited extent. Cr (VI) is easier to absorb than Cr (III) regardless of the contact path. The world health organization (WHO) reports that inhale high amounts of chromium may increase the risk of lung cancer or liver diseases and it causes stomach ulcers (Fawell, 2004). The Environmental Protection Agency (EPA) has set limits for the presence of chromium in drinking water. This standard limit set for chromium by the EPA is 0.05 mg/L (EPA 2010).

Many industrial sectors such as plastics, leather tanning, welding, paint pigments, wood treatments, drilling muds, and copy-machine toners use chromium as a raw material for many different purposes and their wastewater includes chromium. The treatment methods are classified as; chemical extraction (Yao et al. 2019), chemical oxidation-reduction (Huang et al. 2019), reverse osmosis (Mahendra et al. 2017), membrane separation (Laqbaqbia et al. 2019), ion exchange (Cao et al. 2018), adsorption (Cherdchoo et al. 2019) and biosorption (Xining et al. 2015). Many of these methods are not highly

preferred in the industry because the traditional methods can lead to high operating costs of the treatment process and the need for secondary treatment. The biosorption method is one of the commonly used methods for the removal of heavy metal from the aqueous solutions because they are economically more suitable than other processes and provide good quality treatment (El-Reash et al. 2016). Compared with other traditional removal techniques, biosorption is the most applied technique because of its low cost, abundance, high efficiency, and easy-regeneration.

The natural biosorbents are found in huge amounts in many places, and they can easily be modified with some chemicals. Egg powder (Ikram et al. 2016), banana shell (Sharma et al. 2016), walnut shell (Zafarani et al. 2015), cucumber peel (Basu et al. 2017), palm shell (Thangappan et al. 2016), hazelnuts (Karaçetin et al. 2014), garlic stem and horse chestnut shell (Parlayıcı and Pehlivan, 2015) have been applied for the removal of chromium in water sources.

The processing of oak trees in the forest industry reveals a large amount of acorn bark. Acorns, important wildlife in forests, are seeds that are necessary for the renewal of oak trees. It is known that there are approximately 900 types of oak trees in the world on average, and the annually harvested acorn capsule is over 30 million tons (Vinha et al. 2016). The acorn bark is rich in cellulose, lignin and hemicellulose, compared to the vegetable fibers used outside the non-food field. AS is known to have special properties such as strong structure, high chemical stability and strong hydrophobicity (Ishida et al. 2015; Zhang et al. 2018). AS contains lignin, holocellulose, pentosan, tannin and ash and the percentages of them are determined as 34.22%, 56.69, 21.09, 9.18 and 2.56%, respectively (Li et al. 2013).

Cts is a significant amino polysaccharide obtained by deacetylation of chitin which is the most commonly situated biopolymer in the environment after cellulose (Uthaya, 2016). Therefore, Cts contributes significantly to the cellulosic matrix in the real structure and exhibits several perfect chemical properties, such as biocompatibility, being non-toxic, harmful (Wang et al. 2017). One of the advantages of Cts is that it has a renewable structure and is an environmentally friendly natural biopolymer. Recently, it has been used to remove dyes and toxic metal ions from industrial wastewater (Rashid et al. 2017; Wang, 2017). Cts, a cationic polysaccharide, is a linear form with an indiscriminately distributed β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine (Wang, 2017). Cts is a positively charged hydrophilic polymer due to the weak basic groups,. The amino group in the Cts has a value of 6.5 pKa, in this case leading to a protonation with a charge density depending on the pH and % DA in the acidic and neutral solution. Cts has various functional groups such as amino and hydroxyl groups and plays an important role in the biosorption of heavy metal ions by electrostatic attraction or ion exchange (El-Reash et al. 2016). GA was applied as an eco-friendly material for crosslinking. These solid aggregates are biologically functional compounds and are mainly used for chemical modification of polymers (Silve, 2004).

In this study, AS and Cts are not poisonous, cheap and environmental friendly biomaterials. Cts has hydroxyl (-OH) and amino (-NH$_2$) groups in the structure and it increases the efficiency of binding Cr (VI) from the aqueous medium to the surface of composite material. In the biosorption experiment, AS and Cts⊚AS composite were used and their performance was compared by changing such factors as the initial Cr (VI) concentration, pH of the solution, contact time and the amount of biosorbent. The Cts⊚AS composite was used to remove and reduce Cr (VI) in the prepared synthetic wastewater. A model on the isotherm studies was tried for Cr (VI) biosorption and the characteristics of Cts⊚AS composite were conducted before and after treatment using FT-IR. The present study focuses on reducing the concentration of Cr (VI) by biosorption using Cts⊚AS composite. All experiments were carried out in a batch process with the synthetic effluents at ambient conditions. It was concluded that Cts⊚AS composite can find many applications to remove Cr (VI) from industrial wastewater or polluted streams.

2. MATERIALS AND METHOD

Materials and Instruments

The substances used in the experiments are in analytical purity and Cts (average molecular weight), NaOH and K$_2$Cr$_2$O$_7$ are obtained from Sigma-Aldrich. Glutaraldehyde solution (25% in water, v:v), hydrochloric acid, methanol and acetic acid obtained from Merck. For the biosorption experiments, Orion 900S2 Model pH meter, a thermo explicit shaker of GFL 3033 model, and IKAMAG- RO15

model magnetic stirrer were used for simply adjustment of pH and mixing the solutions. The FT-IR spectra for AS, Cts⊙AS composite and Cr (VI) loaded-Cts⊙AS composite were recorded with Bruker-Platinum ATR- vertex 70 (Germany) between 500-4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} using an attenuated total reflection (ATR) accessory. SEM (SEM, Nova Nano SEM 200) is from FEI Company and the samples were covered with a gold layer. The remaining Cr (VI) in the solution was measured by using a UV-Visible Spectrophotometer (Shimadzu UV-1700).

Preparation of Raw Material
Acorns were obtained from Konya-Selcuklu region of Turkey. AS powder particles (125 μm) were prepared in our laboratory and they were washed with pure water and dried at 60 °C in the drying oven. The dried AS was ground in the ball bar grinder. After sieve analysis, the certain powder size between 125-150 μm was used for the experiments.

Preparation of Cts⊙AS Composite
3 g Cts and 1% 300 mL acetic acid solution were stirred with the magnetic mixer until the Cts gelling. Then, 3 g AS was added and then the slurry was stirred about 1 hour continuously until the mixture was homogenous. The prepared mixture was poured into 200 mL, 1 M NaOH solution for coagulation. By adding 6% (V/V) 300 mL ethyl alcohol   solution in the solution, Cts⊙AS composite was obtained (Figure 1.). Cts⊙AS composite was kept about 12 hours in the coagulation solution. After the formation of Cts⊙AS composite, the slurry was filtered. Cts⊙AS is washed with pure water until pH became neutral. The produced Cts⊙AS composite was treated with 3 mL GA and 100 mL methanol solution and they were mixed for 30 min at 70 °C. In this way, with covalent bonds was created and the functional group of the structure was increased at the same time. Cts⊙AS composite was filtered to remove the non-reacted GA solution, and after washing several times with pure water and ethanol, they were left to dry at room temperature for 24 hours. The prepared cross-linked Cts⊙AS composite was stored to evaluate the performance of Cr (VI) removal under the different experimental conditions.
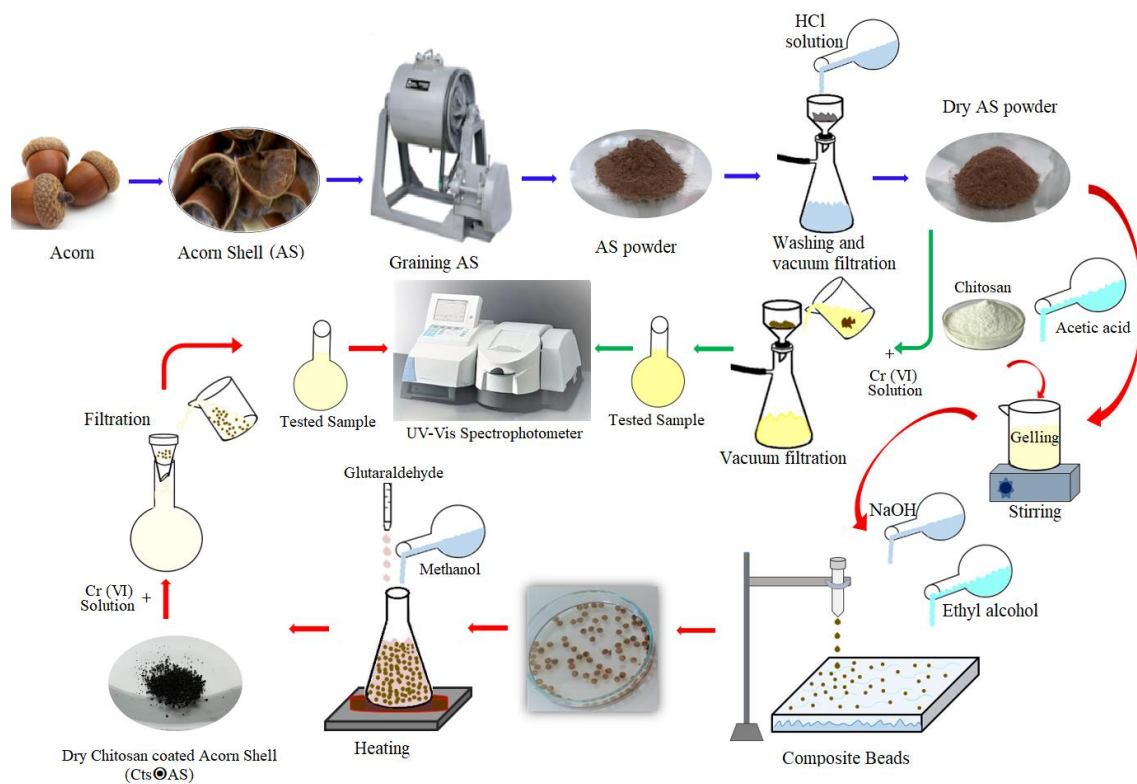

Figure 1. Preparation Schema of Cts⊙AS Composite

Batch Biosorption Studies
The batch method was used to perform the biosorption experiment. The different initial concentrations of Cr (VI) (for AS; 25, 50, 100, 150, 200, 250, 300, 350 ppm; for Cts⊙AS; 25, 50, 100, 150, 200, 300, 400, 500 ppm) were studied and the initial pH of the solution was adjusted to 2. The effect of initial pH on the biosorption was studied by adding 0.1 g AS and 0.05 g Cts⊙AS into a serious of beakers containing 50 ppm Cr (VI) solution and the initial pH from 2 to 6 was adjusted by adding 0.1 M NaOH and 0.1 M HCl solution. The beakers were shaken (200 rpm) at room temperature. After the centrifugation, the residual Cr (VI) concentration in the supernatant liquid was analysed spectrophotometrically at 540 nm using UV-visible spectrophotometer and 1,5 diphenylcarbazide as a complexing agent. This agent reacts with Cr (VI) in a low pH medium and Cr (III)–diphenylcarbazone complex was obtained (Eq. (1)).

$$2CrO_4^{2-} + 3H_4L + 8H^+ \rightarrow Cr(HL)_2^+ + Cr^{3+}H_2L + 8H_2O \tag{1}$$
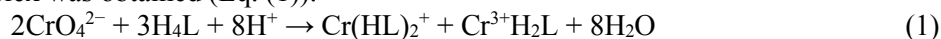
H_4L: 1,5-Diphenylcarbazide
H_2L: Diphenylcarbazone

The percent biosorption of Cr (VI) was calculated as in Eq. (2) below:

$$\% Biosorption = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

$$Biosorption\,Capacity = \frac{C_i - C_f}{m} \times V \tag{3}$$

Where C_i and C_f are the initial and final Cr (VI) concentrations, respectively. The biosorption capacity per unit mass of the biosorbent (q_e) was calculated using Eq. (3).

3. RESULTS AND DISCUSSIONS

Characterization of Cts⊙AS
Figure 2. shows that the FT-IR spectra of AS, Cts⊙AS composite and Cr (VI) loaded Cts⊙AS composite. The spectrum was recorded within the range of 500-4000 cm^{-1}. In the FT-IR spectrum of the AS; the band of the -OH stretching vibrations appeared at 3345 cm^{-1} and the wavelength at 2917 cm^{-1} is caused by the aliphatic C-H stretching vibrations of lignocellulosic components (Yallappa et al. 2017). -COOH indicates strong peaks of strain vibrations at 1608 cm^{-1}. The peak of -C-O vibration at 1020 cm^{-1} wavelength supports the presence in the cellulose and hemicelluloses (Aljoumaa et al. 2017). On the other hand, the FT-IR spectrum of the Cts⊙AS; the alcohol groups (-COH) from the Cts structure appeared at 3353 cm^{-1}, -C-N vibration at 1382 cm^{-1} and -NH$_2$ at 1592 cm^{-1} were related to the vibration in the amide group (Zhou et al. 2014). The peak at 1029 cm^{-1} shows the presence of the ether group corresponding to the form of glutaraldehyde. After the Cr (VI) biosorption on Cts⊙AS; it was seen that some bands shifted and there were changes in the intensity of some bands. –OH, stretching vibrations band shifted from 3353 cm^{-1} to 3291 cm^{-1}, -CH stress band shifted from 2917 cm^{-1} to 2987 cm^{-1}, -NH$_2$ vibration band shifted from 1592 cm^{-1} to 1585 cm^{-1} and increased in the intensity. The intensity of the C-N band at 1382 cm^{-1} wavelength decreased and was divided into 1369 cm^{-1} and 1381 cm^{-1}, the band at 1029 cm^{-1} shifted to 1041 cm^{-1} and it decreased in the intensity. This showed that these changes in the FT-IR spectrum of Cts⊙AS with Cr (VI) biosorption confirm the biosorption of Cr (VI) with the functional groups in Cts⊙AS composite.
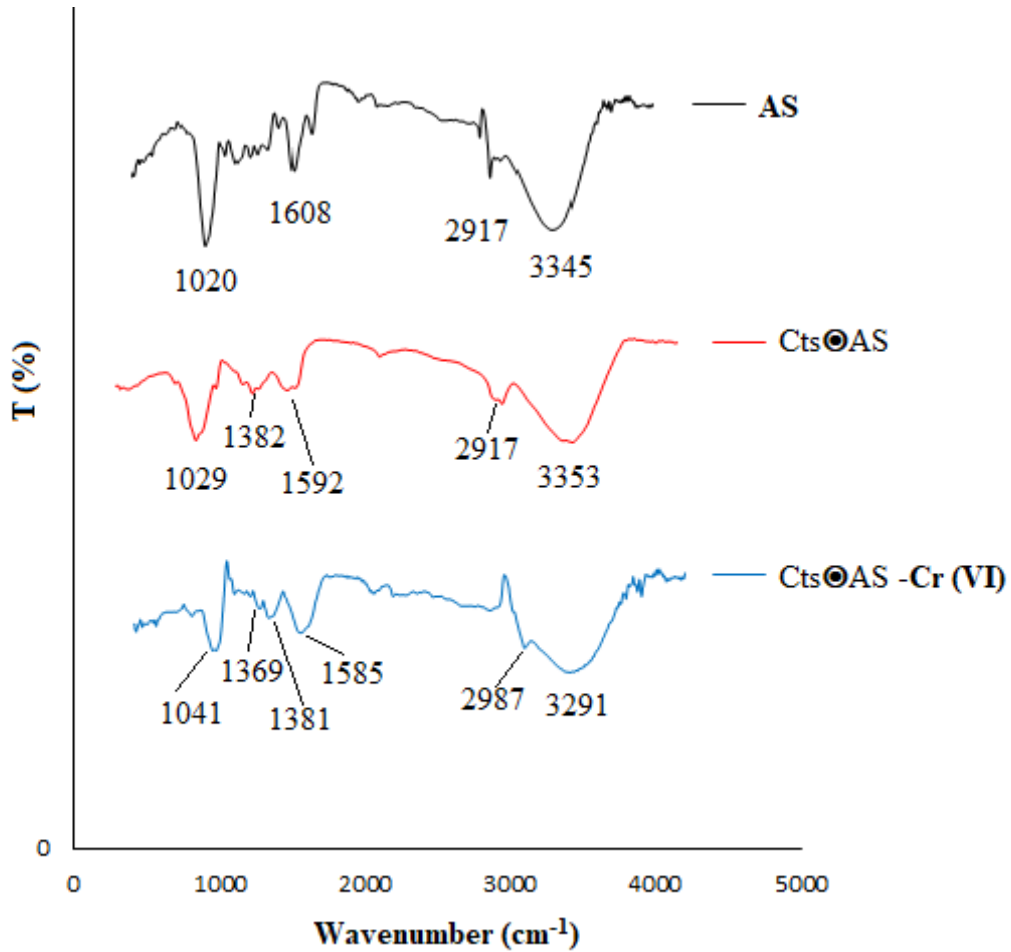
Figure 2. The FT-IR spectral characteristics of AS, Cts◉AS composite and Cts◉AS-Cr (VI)

SEM analysis was made in order to explore the surface morphology of the Cts◉AS composite. The results of the surface morphology of SEM images before and after the biosorption of Cr (VI) are given in Figure 3. After the biosorption of Cr (VI) ions, the surface of the Cts◉AS composite is rough and indented. It is understood that the gaps in this structure are full and the indentation protrusion decreases.
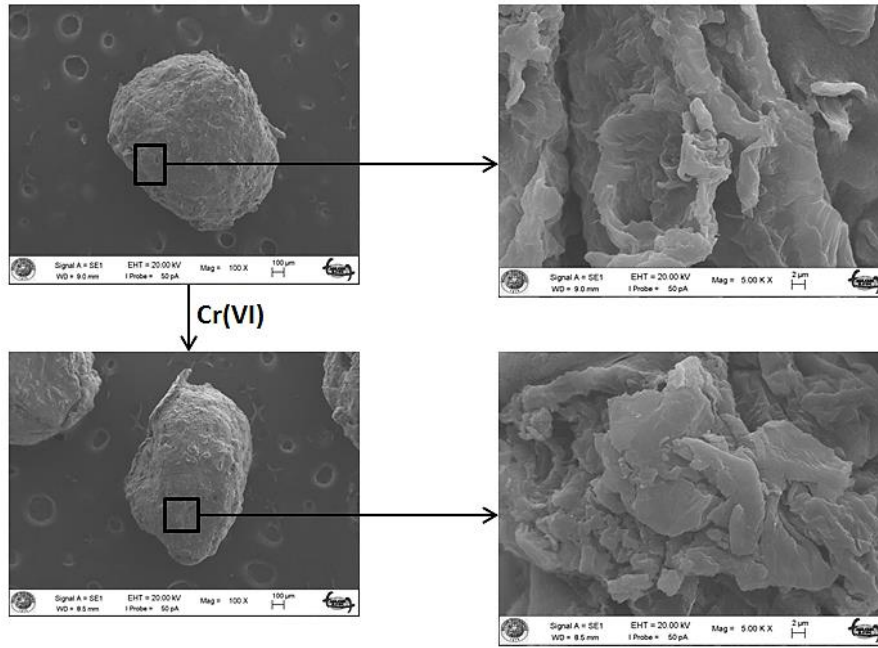
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Figure 3. The SEM images of Cts⊙AS composite before and after Cr (VI) biosorption

Effect of The Cr (VI) Initial Concentration on The Biosorption
The biosorption of Cr (VI) in various concentrations were changed to determine the effect of adsorbate initial concentrations on the biosorption (Figure 4a.). Therefore, 25, 50, 100, 150, 200, 250, 300, 350 ppm Cr (VI) solutions were prepared in the experiments using AS and 25, 50, 100, 150, 200, 300, 400, 500 ppm Cr (VI) solutions were prepared in the experiments using Cts⊙AS composite. The biosorption experiments were carried out by treating the solutions with AS and Cts⊙AS composite. The amount of Cr (VI) remaining in the solution phase by using different concentrations after the filtration was measured with UV-Vis. spectrophotometer. As seen in Figure 4a., as the initial Cr (VI) concentration increased, the biosorption capacity increased. The increase in the capacity was slowed by the fact that the bonding parts in the Cts⊙AS structure were saturated.
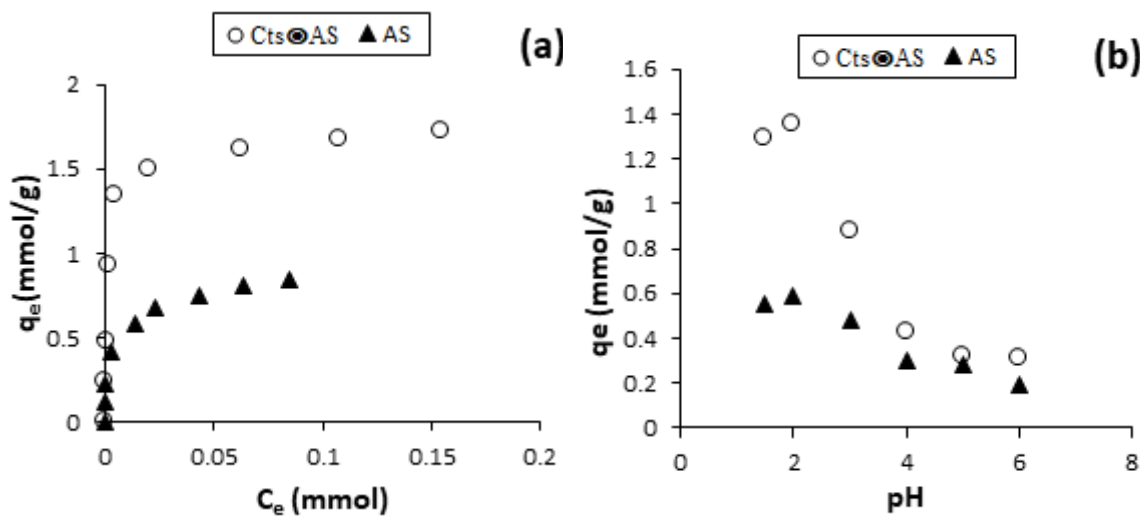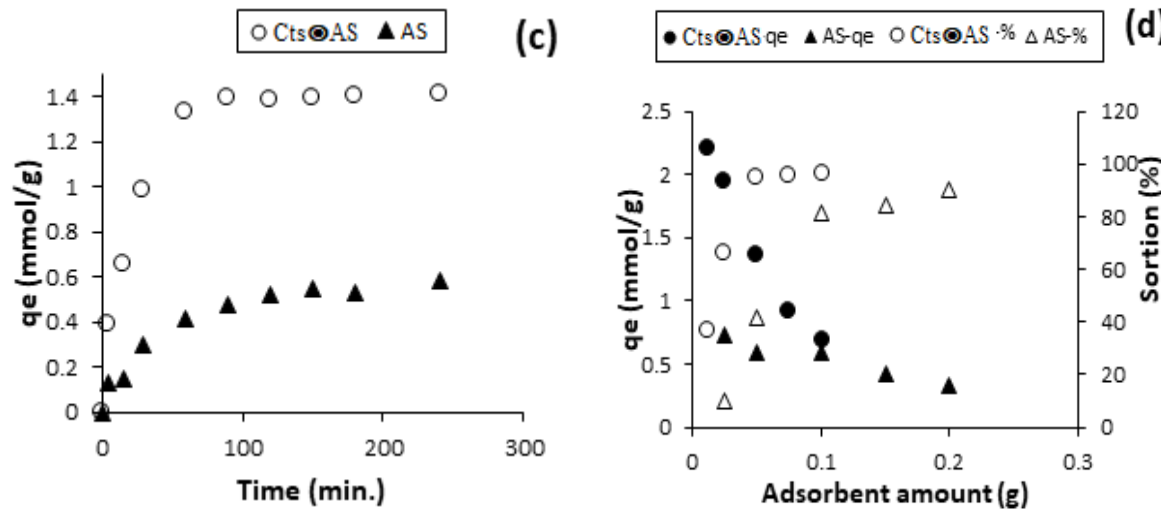
Figure 4. a) Biosorption isotherms of Cr (VI) adsorbed by the AS and Cts◉AS composite **b)** The effect of pH on the biosorption of Cr (VI) by AS and Cts◉AS composite **c)** The effect of contact time on the biosorption of Cr (VI) by AS and Cts◉AS **d)** The effect of biosorbent dosage on the biosorption capacity and the percentage removal of Cr (VI) ions on the biosorption by AS and Cts◉AS composite

Langmuir, Freundlich, Temkin and Scatchard model (Table 1.) were applied for the equilibrium (Eq. (4, 5, 6, 7)). The Freundlich isotherm shows a physical biosorption. According to Freundlich, the Cr (VI) filled sections on the surface of biosorbent are heterogeneous. K_f and n parameters were calculated for Freundlich isotherm. If the n values between 1 and 10 indicating that biosorption is favourable. In this study, n values were found as 4.29 for Cts◉AS composite and 3.33 for AS. The R^2 values obtained from Freundlich isotherm are 0.901 for AS and 0.958 for Cts◉AS composite. Langmuir isotherm expressed chemical and single layer biosorption. This model is defined as the simplest theoretical model for a single layer biosorption. The values of Q_{max} calculated from the Langmuir isotherm of AS, Cts◉AS composite are 44.25 mg/g and 89.29 mg/g, respectively. Hence, the results can be considered to be viable biosorbent for the removal of Cr (VI) from aqueous solutions.

Table 1. Parameters of Langmuir, Freundlich, Scarthard and Temkin Isotherms for Biosorption of Cr(VI) on AS and Cts◉AS Composite

Model	Equation	Eq.	Biosorbent	Parameters for dye				References
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{C_e}{A_s} + \dfrac{1}{K_b A_s}$	(4)	Cts◉AS AS	**A_s** 89.29 44.25	**K_b** 0.29 1.37	**R^2** 0.999 0.995	**R_L** 0.023 0.005	(Langmuir 1918)
Freundlich	$\ln q_e = \ln K_f + \dfrac{1}{n} \ln C_e$	(5)	Cts◉AS AS	**K_f** 28.57 10.40	**n** 4.29 3.33	**R^2** 0.901 0.958		(Freundlich 1906)
Temkin	qe = B lnK_T + B lnCe	(6)	Cts◉AS AS	**B** 10.01 6.07	**K_t** 36.70 6.84	**R^2** 0.942 0.997		(Temkin and Pyzhev 1940)
Scatchard	qe / C_e = Q_s K_s – q_e K_s	(7)	Cts◉AS AS	**Q_s** 84.20 40.99	**K_s** 1.72 0.56	**R^2** 0.942 0.941		(Scatchard 1949)

The R^2 values obtained from Langmuir isotherm plots are 0.999 for Cts◉AS composite and 0.995 for AS (in Table 1). Langmuir isotherm was found to be more suitable for the biosorption. If the value of R_L lies between 0 and 1, the biosorption process is favourable, if R_L is greater than 1, the process is unfavourable. The R_L values received in this study (Table 1.) lies between 0 and 1, which points to a high attraction of Cts◉AS composite and AS for Cr (VI) ions. Temkin isotherm is the model that the

biosorbent–adsorbate interactions into consideration. Temkin isotherm model assumes that the heat of biosorption decreases linearly with coverage due to the biosorbent–adsorbate interactions and the biosorption is characterized by a uniform distribution of binding energies. Both K_T and B can be determined from a plot q_e vs. ln C_e (Figure 5.) and the constants were determined from the intercept and slope, respectively. The related parameters are presented in Table 1. To evaluate and compare the saturation capacities of the composite toward the Cr (VI) ions, the biosorption isotherms were analysed and fitted using the Scatchard equation (Figure 5.). When the Scatchard plot showed a deviation from linearity, greater emphasis was placed on the analysis of the biosorption data in terms of the Freundlich model, in order to construct the biosorption isotherms of the Cr (VI) at particular concentrations in the solution. In the biosorption of Cr (VI) ions, Scatchard analysis of the equilibrium binding data for Cr (VI) on the composite gave rise to a linear plot, indicating that the Langmuir model could be applied. The biosorption capacity of Cr (VI) onto the AS and Cts◉AS composite were compared with other biosorbents reported in the literature and are summarized with their maximum Cr (VI) biosorption capacity in (Table 2.). It is easy to find that the biosorption of AS and Cts◉AS composite are better than other agricultural waste biosorbents in (Table 2.) which fully demonstrate the successful of Cr (VI) elimination.

Table 2. Biosorption Capacity of AS and Cts◉AS Composite Compared to The Other Published Low-Cost Biosorbents for Cr (VI) Removal

Biosorbent material	Q_{max} (mg/g)	References
Rubber leaves	22.97	(Nag et al. 2015)
Pistachio shell	27.95	(Banerjee et al. 2018)
Anthill-eggshell composite	12.99	(Yusuff et al. (2018)
Potato peels	1.97	(Mohammed et al. 2017)
Tea waste	7.29	(Sharma et al. 2016)
Peanut hull	14.13	(Ali et al. 2016)
Cts particles	31.4	(Dima et al. 2015)
Chestnut shell	4.44	(Niazi et al. 2018)
AS	**44.25**	**This study**
Cts◉AS composite	**89.29**	**This study**

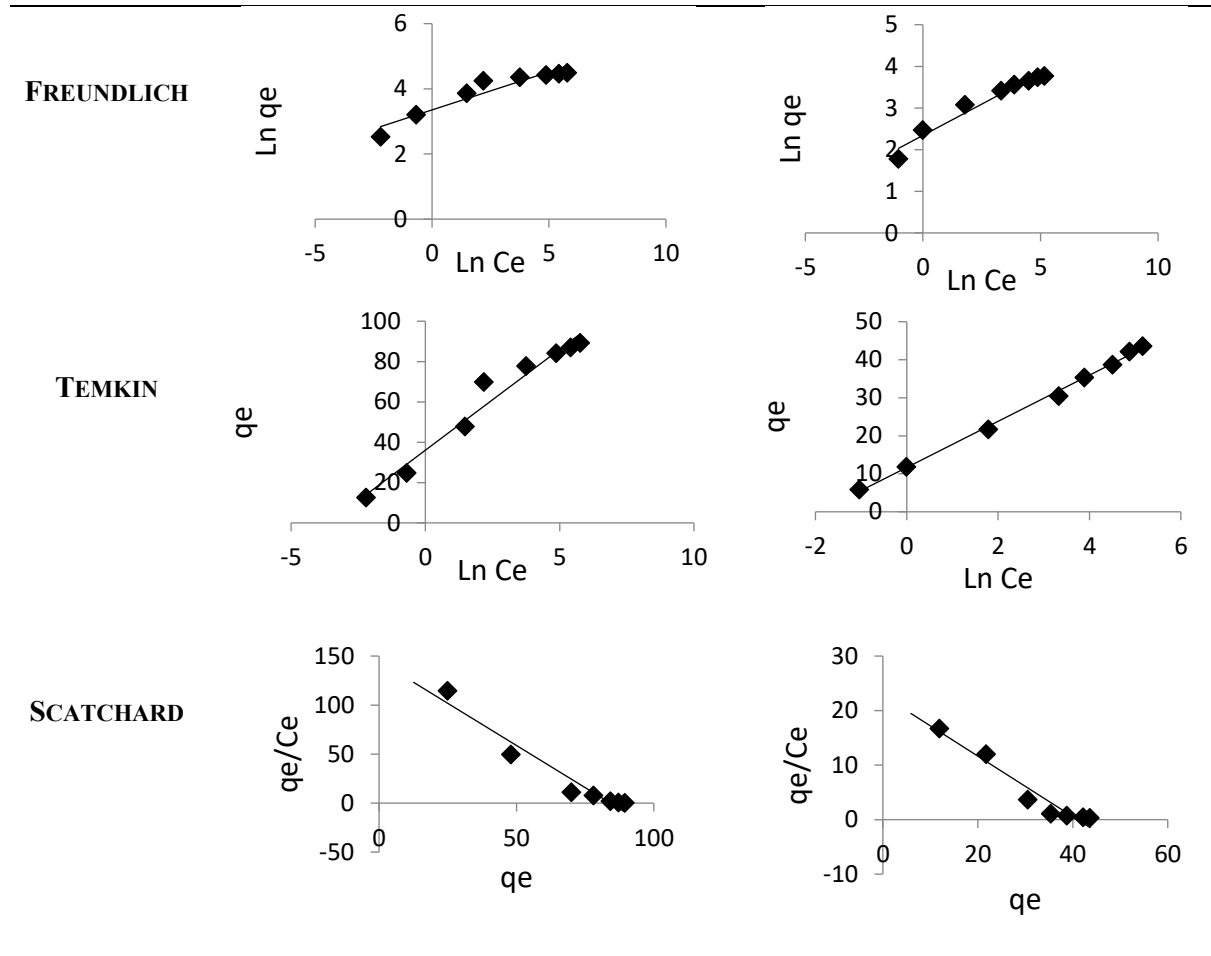| ISOTHERMS	CTS◉AS	AS
LANGMUIR		

FREUNDLICH
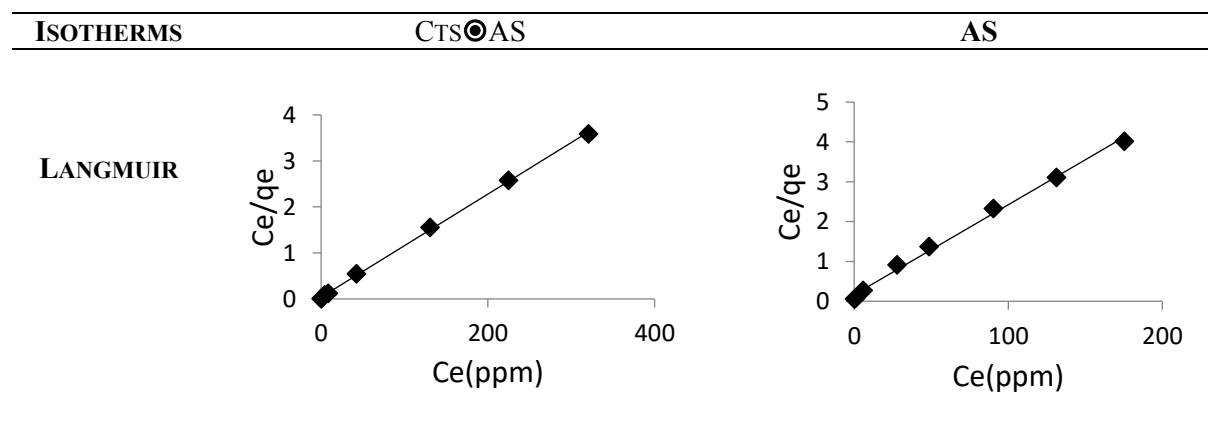
TEMKIN

SCATCHARD

Figure 5. Langmuir, Freundlich Temkin and Scatchard models for the biosorption of Cr (VI) onto AS and Cts◉AS composite.

Effect of pH on The Biosorption

The change in the pH value of the solution affects the biosorption sites on the biosorbent surface and the charge profiles of the adsorbate, thus significantly affecting the biosorption. The solution phase was considered in the different pH values (1.5, 2, 3, 4, 5, 6) for the biosorption of Cr (VI). The distinctive mechanical, chemical and electrical properties of interfaces of the solid and solution phase create great and highly varied effects on the biosorbent behaviour. The surface layer of the Cts◉AS composite and AS exhibits an electrical charge effect in the response section of Cr (VI) and the biosorbent. The interfaces dividing electrically neutral bulk phases can appear to bear a charge, positive or negative charges spread relative to the biosorbent and Cr (VI) interface, resulting in the formation of an electrical double layer (Berg, 2010). The change in the biosorption capacities of Cr (VI) ions against pH change from the results is plotted in Figure 4b. The acidity of the solution is effective in the biosorption of Cr (VI) since it will be able to race between the Cr (VI) with H^+ ions to the active areas on the AS and Cts◉AS composite surfaces. The biosorption capacity of Cr (VI) at pH 6 was 0.52 mmol/g and increased to 0.59 mmol/g at pH 2 for the AS. On the other hand, the biosorption capacity of Cr (VI) at pH 6 was 1.28 mmol/g and increased to 1.36 mmol/g at pH 2 for the Cts◉AS composite. In the biosorption experiments, the biosorption values of Cr (VI) ions were found to be maximum around pH 2 for the pH range 1.5-6.0. The similar pH-depended trend was also observed by some other researchers for the Cr (VI) removal by various biosorbents (Koushkbaghi et al. 2018; Khalid et al. 2018). The better biosorption capability discovered at a low hydrogen ion concentration value is related to a large number of H^+ ions present at around low pH values, which successively neutralize the negatively charged hydroxyl groups (–OH) ions causing an increasing hindrance to the diffusion of positively charged dichromate ions. Once increasing pH values from 2.0 to 6.0, $HCrO_4^-$ gradually converts to the divalent

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CrO_4^{2-}. The amine groups ($-NH_2$) in Cts are mainly responsible for Cr (VI) biosorption and can be protonated to NH_3^+ in a slightly acidic medium (Salih & Ghosh, 2018). As pH increases, the surface of biosorbent become a lot of negatively charged ions and therefore, the number of positively charged sites diminished. This causes an increased repulsion between Cr (VI) and AS or Cts◉AS composite. A negatively charged surface site on the biosorbent doesn't favour the biosorption of Cr (VI) because of the static repulsion. Adjusting the pH of the solution greater than 6.0 by adding NaOH causes flocculation and deprotonation of the biosorbent (Rinaudo, 2006). Additionally, pH lower than 1.5; the amine group of Cts is easily protonated and which causes electrostatic repulsion to Cr (VI) ion.

The Effect of Contact Time on The Biosorption of Cr (VI)
The effect of contact time on the biosorption of Cr (VI) in the biosorption experiments using AS and Cts◉AS composite is shown in Figure 4c. In this study, 25 mL, 150 ppm Cr (VI) solution was added to 0.1 g of AS and 0.05 g of Cts◉AS composite, separately for the biosorption process. The mixture was stirred in the magnetic stirrer at the specified time intervals (5, 15, 30, 60, 90, 120, 180, 240 min) and the Cr (VI) contents of the remaining solution after the filtration were measured with the UV-Vis spectrometer. As seen in Figure 4c., the biosorption of Cr (VI) into AS increased rapidly in the first 5-30 min. and then reached the equilibrium between 30-120 min. The longer contact time was not effective on the biosorption, and the contact time was taken as 120 minutes. On the other hand, Cr (VI) adsorption on the Cts◉AS composite increased rapidly in the first 5-30 min. and then reached a stable value in 30-90 min. The longer contact time was not effective on the biosorption, and the contact time was taken as 90 minutes. It has been observed that the biosorption is fixed to the point of reaching the equilibrium for both of them. Due to the large surface area of the Cts◉AS composite/AS and the existence of functional groups in the matrix, the first part (15 min.) of the biosorption is fast because Cr (VI) ions tend to interact with the functional groups of the biosorbent. At the end of the applied contact time, the optimum time was determined as 120 min for the AS and 90 min. for Cts◉AS composite. It was seen that the Cts◉AS composite reached the equilibrium in a shorter time compared to the AS.

Effect of The Biosorbent Dose on The Biosorption
An optimal biosorbent dose should be determined to maximize the interactions between the Cr (VI) and biosorption sites of the AS and Cts◉AS composite in the solution phase. The relationship between the AS and Cts◉AS composite dose and the biosorption capacity, as much as the removal efficiency of Cr (VI), are illustrated in Figure 4d. 0.025; 0.050; 0.100; 0.150 and 0.200 g of the weighed AS were separately bottled and 150 ppm of 25 ml of Cr (VI) solutions were added, then stirred for 120 minutes at 200 rpm in a magnetic stirrer. On the other hand, 0.012; 0.025; 0.050; 0.075 and 0.100 g of the weighed Cts◉AS were separately bottled and 150 ppm of 25 ml of Cr (VI) solutions were added then stirred for 90 minutes at 200 rpm in the magnetic stirrer. Cr (VI) contents of the remaining solution after the filtration were measured with the UV-Vis spectrometer. The results of the experiment (Figure 4d.) showed that the biosorption process is strongly dependent on these parameters. A relatively slow increase in the biosorbent amount range of 0.012 - 0.1 g Cts◉AS, Cr (VI) removal (R, %) from 36.63 to 95.93% was achieved and slow increase in the biosorbent amount range of 0.025-0.2 g AS, Cr (VI) removal (R, %) from 10.28 to 90.32% was achieved. The biosorption capacity of Cr (VI) follows with the increase of biosorbent dose and a tendency has been observed in the biosorption process of AS and Cts◉AS composite. Therefore, the biosorption capacity of AS decreases from 2.20 to 0.67 mmol/g by increasing the biosorbent rate between 0.012 and 0.1 g and the biosorption capacity of AS decreases from 0.72 to 0.33 mmol/g by increasing the biosorbent rate between 0.025 and 0.2 g. The maximum biosorption mass was found as 0.05 g and 0.1 g for Cts◉AS composite and AS, respectively.

CONCLUSION
The AS and a new Cts◉AS composite was designed to be an effective biosorbent for the biosorption of Cr (VI) from aqueous solutions. The biosorption behavior of Cr (VI) onto AS and Cts◉AS composite was investigated and it was found to be dependent on pH, biosorbent dosage, initial Cr (VI) concentration and contact time. The functional groups such as amino, carboxyl and hydroxyl groups on the surface of Cts◉AS played an important role in the binding of Cr (VI) from the medium. Langmuir, Freundlich, Stachard and Temkin isotherms were tried and the biosorption constants were calculated.

Langmuir isotherm model best described the biosorption process (R^2 is 0.99) and the values of the R_L factor indicating a strong binding at the active sites of the Cts◉AS composite. By applying the Langmuir model equation, the maximum Cr (VI) capacities of Cts◉AS composite and AS were found to be 89.29 and 44.25 mg/g, respectively. Cts◉AS composite displayed a higher biosorption capacity than AS. The biosorption studies revealed that the optimum contact time for the equilibrium was found to be 90 min. and 120 min. for Cts◉AS and AS, respectively. pH 2 was an optimum value for the biosorption of Cr (VI). The coordination, electrostatic attraction and complexation of Cr (VI) with the functional groups can be accepted for the interaction. Cts◉AS is recommended for the treatment plants to remove the toxic Cr (VI) species from effluents. The produced biosorbent was generated from natural sources that claim it is an environmental friendly biosorbent for the application of Cr (VI) removal from the polluted solution.

REFERENCES
Ali, R. M., Hamad, H. A., Hussein, M. M. and Malash, G. F., 2016, Potential of using green biosorbent of heavy metal removal from aqueous solutions: Biosorption kinetics, isotherm, thermodynamic, mechanism and economic analysis, *Ecological Engineering*, 91, 317–332.

Aljoumaa, K., Tabeikh, H. and Abboudi, M., 2017, Characterization of apricot kernel shells (Prunus armeniaca) by FTIR spectroscopy, DSC and TGA, *Journal of the Indian Academy of Wood Science*, 14(2), 127–132.

Basu, M., Guha, A. K. and Ray, L., 2017, Biosorption of Lead on Cucumber Peel, *Journal of Cleaner Production*, 151 603–615.

Banerjee, M., Bar, N., Basu, R. K. and Das., S. K., 2017, Comparative study of adsorptive removal of Cr(VI) ion from aqueous solution in fixed bed column by peanut shell and almond shell using empirical models and ANN, *Environmental Science and Pollution Research*, 24, 10604–10620.

Banerjee, M., Bar, N., Basu, R. K. and Das, S. K., 2018, Removal of Cr(VI) from its aqueous solution using green biosorbent pistachio shell: a fixed bed column study and GA-ANN modeling, *Water Conservation Science and Engineering*, 3, 19–31.

Berg, J. C., 2010, An introduction to interfaces & colloids: the bridge to nanoscience, *World Science*.

Cao, W., Wang, Z., Ao, H. and Yuan, B., 2018, Removal of Cr(VI) by corn stalk based anion exchanger: the extent and rate of Cr(VI) reduction as side reaction, *Colloids and Surfaces A*,539, 424–432.

Cherdchoo, W., Nithettham, S. and Charoenpanich, J., 2019, Removal of Cr(VI) from synthetic wastewater by biosorption onto coffee ground and mixed waste tea, *Chemosphere*, 221, 758–767.

Dima, J. B., Sequeiros, C. and Zaritzky, N. E., 2015, Hexavalent chromium removal in contaminated water using reticulated Cts micro/nanoparticles from seafood processing wastes, *Chemosphere*, 141, 100–111.

El-Reash, Y. A., 2016, Magnetic Cts modified with cysteine-glutaraldehyde as biosorbent for removal of heavy metals from water, *The Journal of Environmental Chemical Engineering*, 4(4), 3835–3847.

Fawell, J. K., Lund, U. and Mintz, B., 2004, Chromium in Drinking-water, *Background document for development of WHO Guidelines for Drinking Water Quality*.

Freundlich, H. M. F., 1906, Over the biosorption in solution, *The Journal of Physical Chemistry*, 57, 385–471.

Ghasemi, M., Ghoreyshi, A. A., Younesi, H. and Khoshhal, S., 2015, Synthesis of a high characteristics activated carbon from walnut shell for the removal of Cr(VI) and Fe(II) from aqueous solution: single and binary solutes biosorption, *Iranian Journal of Chemical Engineering*, 12(4), 28–51.

Huang, Z., Dai, X., Huang, Z., Wang, T., Cui, L., Ye, J. and Wu, P., 2019, Simultaneous and efficient photocatalytic reduction of Cr(VI) and oxidation of trace sulfamethoxazole under LED light by rGO@Cu2O/ BiVO4 p-n heterojunction composite, *Chemosphere*, 221, 824–833.

Ikram, M., Rehman, A. U., Ali, S., Ali, S., Bakhtiar, S. U. I. H. and Alam, S, 2016, The adsorptive potential of chicken egg shells for the removal of oxalic acid from wastewater, *Journal of Biomedical Engineering*, 2(2), 118–131.

Ishida, Y., Hirota, T., Sato, S., Kamegai, M., Kim, S. K., Park, S. Y., Koo, D. H., Shon, M. S., Kim, G. N., Park, H. R. and Lee, S. C., 2015, Discriminative analysis of free and esterified gallic acids in

acorn shells by thermochemolysis-gas chromatography/mass spectrometry in the presence of organic alkalis, *Journal of Analytical and Applied Pyrolysis*, 116, 114–119.

Karaçetin, G., Sivrikaya, S. and Imamoğlu, M., 2014, Biosorption of methylene blue from aqueous solutions by activated carbon prepared from hazelnut husk using zinc chloride. *Journal of Analytical and Applied Pyrolysis* ,110:70–276.

Koushkbaghi, S., Zakialamdari, A., Pishnamazi, M., Ramandi, H. F., Aliabadi, M. and Irani, M., 2018, Aminated-Fe3O4 nanoparticles filled Cts/PVA/PES dual layers nanofibrous membrane for the removal of Cr (VI) and Pb (II) ions from aqueous solutions in biosorption and membrane processes, *Chemical Engineering Journal*, 337, 169–182.

Khalid, R., Aslam, Z., Abbas, A., Ahmad, W., Ramzan, N. and Shawabkeh, R., 2018, Adsorptive potential of Acacia nilotica based biosorbent for chromium (VI) from an aqueous phase, *Chinese Journal of Chemical Engineering*, 26(3), 614–622.

Langmuir, I., 1918, The biosorption of gases on plane surfaces of glass, mica and platinum, *Journal of the American Chemical Society*, 40(9), 1361–1403.

Laqbaqbia, M., García-Payoa, M. C., Khayeta, M., El Kharrazc, J. and Chaouchb, M., 2019, Application of direct contact membrane distillation for textile wastewater treatment and fouling study, *Separation and Purification Technology*, 209, 815–825.

Li, S., Wang, C., Chu, F., Xia, J. and Xu, Y., 2013, Effect of compatibilizers on composites of acorn shell powder and low density polyethylene Acorn shell/LDPE composites, *Bioresources*, 8(4), 5817–5825.

Mohammed, N. M. S. and Salim, H. A. M., 2017, Biosorption of Cr (VI) Ion from Aqueous Solutions by Solid Waste of Potato Peels, *Science Journal of University of Zakho*, 5(3), 254–258.

Nag, S., Mondal, A., Mishra, U., Bar, N. and Das, S. K., 2015, Removal of chromium(VI) from aqueous solutions using rubber leaf powder: batch and column studies, *Desalination Water Treatment*, 57, 16927–16942.

Niazi, L., Lashanizadegan, A. and Sharififard, H., 2018, Chestnut oak shells activated carbon: Preparation, characterization and application for Cr (VI) removal from dilute aqueous solutions, *Journal of Cleaner Production*, 185, 554–561.

Parlayıcı, Ş. and Pehlivan, E., 2015, Natural biosorbents (garlic stem and horse chesnut shell) for removal of chromium(VI) from aqueous solutions, *Environ Monit Assess*, 187, 763.

Rashid, S., Shen, C., Yang, J., Liu, J. and Li, J., 2018, Preparation and properties of Cts–metal complex: Some factors influencing the biosorption capacity for dyes in aqueous solution, *Journal of Environmental Sciences*, 66, 301–309.

Rinaudo, M., 2006, Chitin and Cts: Properties and applications, *Progress in Polymer Science*, 31,603–632.

Saka, C., Sahin, Ö., Adsoy, H. and Akyel, S. M., 2012, Removal of Methylene Blue from Aqueous Solutions by using Cold Plasma, Microwave Radiation and Formaldehyde Treated Acorn Shell, *Separation Science and Technology*, 47, 1542–1551.

Salih, S. S. and Ghosh, T. K., 2018, Preparation and Characterization of Cts-Coated Diatomaceous Earth for Hexavalent Chromium Removal, *Environmental Processes*, 5, 23–39.

Scatchard, G., 1949, The attractions of proteins for small molecules and ions, *Annals of the New York Academy of Sciences*, 51, 660–672.

Sharma, P. K., Ayub, S. and Tripathi, C. N., 2016, Isotherms describing physical biosorption of Cr(VI) from aqueous solution using various agricultural wastes as biosorbents, *Cogent Engineering*, 3, 1186857.

Sivakami, M. S., Gomathi, T., Venkatesan, J., Jeong, H. S., Kim, S. K. and Sudha, P. N., 2013, Preparation and characterization of nano Cts for treatment wastewaters, *International Journal of Biological Macromolecules*, 57, 204–212.

Subbaiah, M. V. and Kim, D. S., 2016, Biosorption of methyl orange from aqueous solution by aminated pumpkin seed powder: kinetics, isotherms, and thermodynamic studies, *Ecotoxicology and Environmental Safety*, 128, 109–17.

Sivakami, M. S., Gomathi, T., Venkatesan, J., Jeong, H. S., Kim, S. K. and Sudha, P. N., 2013, Preparation and characterization of nano Cts for treatment wastewaters, *International Journal of Biological Macromolecules*, 57, 204–212.

Silva, C. J. S. M., Sousa, F., Gübitz, G. and Cavaco-Paulo, A., 2004, Chemical modifications on proteins using glutaraldehyde, *Food Technolgy and Biotechnolgy*, 42(1), 51–56.

Temkın, M. J. and Pyzhev, V., 1940, Recent modifications to Langmiur isotherms, Acta Physiochim, *USSR*, 12, 217–222.

Thangappan, H., Parambathu, A. V. and Joseph, S., 2016, Surface characterization and methylene blue biosorption studies on a mesoporous biosorbent from chemically modified Areca triandra palm Shell, *Desalination Water and Treatment*, 44(57), 21118–21129.

US EPA, 2010, IRIS Toxicological Review of Hexavalent Chromium External Review Draft), *US Env Prot Age Wash DC EPA/635/ R- 10/004A*.

Uthaya, J. and Annadurai, G., 2016, Cts and Cts nanoparticle synthesis basic inroduction, *Research scholar U/G Dr. G. Annadurai Sri Paramakalyani Centre for Env* Sci.

Vinha, A. F., Barreira, J. C. M., Costa, A. S. G. and Oliveira, M. B. P. P., 2016, A New Age for Quercus spp. Fruits: Review on Nutritional and Phytochemical Composition and Related Biological Activities of Acorns, *Comprehensive Reviews in Food Science and Food Safety*, 15, 1541–4337.

Yallappa, S., Deepthi, D. R., Yashaswin, S., Hamsanandini, R., Chandraprasad, M., Kumar, S. A. and Hegde, G., 2017, Natural biowaste of Groundnut shell derived nano carbons: Synthesis, characterization and its in vitro antibacterial activity, *Nano-Structures & Nano-Objects*, 12, 84–90.

Yao, L., Zhu, Y., Xu, W., Wang, H., Wang, X., Zhang, J., Liu, H. and Lin, C., 2019, Combination of dispersive solid phase extraction with dispersive liquid–liquid microextraction for the sequential speciation and preconcentration of Cr(III) and Cr(VI) in water samples prior to graphite furnace atomic absorption spectrometry determination, *Journal of Industrial and Engineering Chemistry*, 72, 189–195.

Yusuff, A. S., Gbadamosi, A. O., Lala, M. A. and Ngochindo, J. F., 2018, Synthesis and characterization of anthill-eggshell composite biosorbent for removal of hexavalent chromium from aqueous solution, *Environmental Science and Pollution Research*, 25, 19143–19154.

Zafarani, H. R., Bahrololoom Mo, E., Noubactep, C. and Tashkhourian, J., 2015, Green walnut shell as a new material for removal of Cr(VI) ions from aqueous solutions, *Desalination Water and Treatment*, 55, 431–439.

Zakzeski, J., Bruijnincx P. C. A., Jongerius, A. L. and Weckhuysen, B. M., 2010, The catalytic valorization of lignin for the production of renewable chemicals, *Chemical Reviews*, 110(6), 3552–3599.

Zhang, Y., Yang, L., Wang, D. and Li, D, 2018, Structure elucidation and properties of different lignins isolated from acorn shell of Quercus variabilis Bl. *International Journal of Biological Macromolecules*, 107, 1193–1202.

Zheng, J., Vemuri, R. S., Estevez, L., Koech, P. K., Varga, T, Camaioni, D. M., Blake, T. A., McGrail, B. P. and Motkuri, R. K., 2017, Pore-Engineered Metal-Organic Frameworks with Excellent Biosorption of Water and Fluorocarbon Refrigerant for Cooling Applications, *Journal of the American Chemical Society*, 139(31), 10601–10604.

Zhou, Z., Lin, S., Yue, T. and Lee, T. C., 2014, Biosorption of food dyes from aqueous solution by glutaraldehyde cross-linked magnetic Cts nanoparticles, *Journal Food Engineering*, 126, 133–141.

Xining, S., Jingjing, M., Zengqiang, Z. and Zhiyong, Z., 2015, Biosorption of hexavalent chromium from aqueous medium with the antibiotic residue, *Advance Journal of Food Science and Technology*, 7, 120–128.

Wang, B., Zhu, Y., Bai, Z., Luque, R. and Xuan, J., 2017, Functionalized Cts biosorbents with ultra-high performance, mechanical strength and tunable selectivity for heavy metals in wastewater treatment, *Chemical Engineering Journal* 325:350–359.