

# PREPARATION AND APPLICATION OF GLUTARALDEHYDE CROSS-LINKED CHITOSAN COATED BENTONITE CLAY CAPSULES: CHROMIUM(VI) REMOVAL FROM AQUEOUS SOLUTION

TÜRKAN ALTUN \*

*Department of Chemical Engineering, Konya Technical University, Konya 42150, Republic of Turkey*

## ABSTRACT

New sources in literature have explained that more efficient biosorbents can be developed from natural adsorbents. One of the methods to make these natural adsorbents more efficient is preparation of composites. Hydroxyl (-OH) and amino (-NH<sub>2</sub>) groups within the structure of chitosan leads adsorbents to have a binding potential with heavy metals. In this study, a composite adsorbent made of chitosan and bentonite clay was prepared. Bentonite clay and chitosan-coated Bentonite clay composite capsules (BC) were characterized in terms of FTIR and SEM analysis. (BC) composite adsorbent was used for the adsorption of Cr(VI) ions from aqueous solution. The effects of some parameters such as pH, adsorbent dosage, adsorbate concentration, temperature and contact time on the adsorption of Cr(VI) on BC were investigated with batch studies. In order to evaluate the experimental data, Langmuir, Freundlich, Scatchard and Dubinin-Radushkevich (D-R) adsorption isotherm models were used for the analysis of adsorption equilibrium. The adsorption process was well fitted to Scatchard adsorption isotherm. While bentonite clay had 11,076 mg/g maximum adsorption capacity, BC composite had 106.444 mg/g maximum adsorption capacity for the removal of Cr(VI) ions (25 °C, pH 2, contact time 60 minutes). It was concluded that chitosan-bentonite composite adsorbent can be effectively used for the removal of Cr(VI).

**Keywords:** Composite, Chitosan, Bentonite clay, Cr(VI), Adsorption, Isotherm.

## 1. INTRODUCTION

Various pollutants such as organic compounds, heavy metals and oxyanions emerge as a result of industrial applications. Especially organic pollution combining with heavy metals should be taken into consideration as an important problem in terms of environment. Since these pollutants and their derivatives are carcinogenic and have toxic effect on humans, animals as well as aquatic plants and animals, they should be removed via wastewater treatment methods. Among these methods, adsorption is known as the most economic and effective treatment method [1, 2]. In order to obtain an efficient adsorption process, selection of an appropriate adsorbent is very important. Depending on the surface properties, most of the adsorbents can just remove either organic pollutants or heavy metals [3]. For this reason, instead of using different adsorbents, alternative adsorbent materials are required to remove both organic pollutants and heavy metals at the same time.

Since time immemorial, the clays have been an important part of human life. The clays attract attention with their wide area of usage from decorative belongings to adsorption, cement production, filtration and nanocomposite production with developing technology. The clays are preferred as an adsorbent for the removal of many pollutants since they are cheap and they have good properties even at very low amounts. Montmorillonite clay, as a well-known important one, has a very high surface area. It might adsorb pollutants in higher amounts when compared to other clay minerals [1, 4, 5].

The main component of bentonite is montmorillonite clay which determines its properties. Bentonite is frequently formed by variation of volcanic ash. It is mainly consisting of smectite minerals. The general form of smectite minerals is montmorillonite clay. Bentonite has a chemical structure consisting of silicium and aluminum (silicon and aluminum) (Al<sub>2</sub>O<sub>3</sub>.4SiO<sub>2</sub>.H<sub>2</sub>O). Bentonite has a wide range of usage fields such as a binding agent for mould preparation in iron casting, as a waste adsorber in cat litter, as a binding agent for iron ore pellet production, as pollutant remover in oil production, as animal feed supplement, as filling material in pharmaceutical and cosmetic industry, as adsorbent, in detergent and liquid soap production, paper manufacturing as well as dye and lustering process [6].

Due to toxic and carcinogenic effects of heavy metals on humans and living things in aquatic environment, heavy metal pollution has attracted attention [7]. Recently, accelerating industrialization has resulted in increase and accumulation of Cr(VI) ions which is one of the most commonly found metals in water and environment. Chromium is generally used as corrosion control agent for dye and pigment production, leather tanning process, electroplating industry, metal cutting process, explosive material manufacturing, mining and ore processing activities, metallurgical industry, etc. [7]. In the wastes of these industrial processes, generally toxic amount of Cr(VI) mixes with sewage.

Depending on the pH of waste solution, Cr(VI) can be found in the forms of (Cr<sub>2</sub>O<sub>7</sub>)<sup>2-</sup>, (HCr<sub>2</sub>O<sub>7</sub>)<sup>-</sup>, (HCrO<sub>4</sub>)<sup>-</sup> and (CrO<sub>4</sub>)<sup>2-</sup>. This creates serious threats for both human and environmental health [8].

The main treatment methods for the removal of Cr(VI) ions are chemical precipitation, reverse osmosis, ion exchange and adsorption. Chemical precipitation method has some disadvantages like production of toxic chemical treatment sludge, requiring chemicals continuously and having a very high operating cost. Moreover, reverse osmosis and ion exchange with commercial resins have limited usage since they have also high investment and operating costs as well as they need qualified staff in reverse osmosis for the control of process. However, removal of heavy metals from aqueous solutions by using adsorption method with low-cost adsorbents might be both economic and effective [9]. For the removal of Cr(VI), very little costly organic waste materials such as agricultural and industrial wastes [10–12], natural clays [4, 13, 14] and activated carbon [15] and the composites of these natural adsorbents can be used. In recent years, the researchers have tried various composite production methods in order to activate the adsorbents. It was observed that formation of different composites from natural adsorbents activated them and their adsorption capacities increased [16–18].

Heavy metal adsorption process with clays is a significant treatment technology that does not lose its importance. However, adsorption with natural clays might take longer time. Formation of clays with biosorbents such as chitosan increased the alternatives for new adsorbents. For this aim, clay composites are synthesized by different methods. Both clay and chitosan can be found easily in nature. For clay-chitosan composites, the disadvantages mentioned previously disappear and they can be used for heavy metal removal from aqueous solutions successfully with a certain performance. In addition to this, there are studies related with heavy metal removal from wastewater by these adsorbents [19–22]. Hydroxyl (-OH) and amino (-NH<sub>2</sub>) groups in the structure of chitosan have a potential to make bonds with heavy metals [23]. Therefore, the adsorption performance of BC prepared as a composite was investigated for the removal of Cr(VI) ions from aqueous solution.

In the literature, there are available adsorbents prepared with different methods and different bentonite clays and applications of these adsorbents. In the literature, related to bentonite; Cr(VI) adsorption with chitosan/bentonite composite [19], preparation and characterization of bentonite-chitosan nano composite [24], removal of different impurities (dyes, phenolic compounds, fluoride, metals and ions) from aqueous solutions with various chitosan-bentonite nanocomposites [25], comparative and competitive adsorption of copper, lead and nickel with powder adsorbent chitosan immobilized on bentonite [26], use of chitosan impregnated modified bentonite as an adsorbent for remediation of oil spill from aqueous solution [27], Mn<sup>2+</sup> modified bentonite

for the removal of fluoride from aqueous solution [1], performance of 5% bentonite/chitosan nanocomposite in the removal of Cr(VI) ions from wastewater [18], removal of Pb (II) by magnetic bentonite prepared from Fe<sub>3</sub>O<sub>4</sub> and bentonite [28], bilateral adsorption of silver and copper onto bentonite, adsorption of indium (III) ions from aqueous solution using chitosan coated bentonite beads [29] studies are available.

Although there are studies about bentonite in the literature, there is no study in the literature about the removal of Cr (VI) from aqueous solutions by chitosan coated bentonite clay capsules (BC) used in this study. In this present study, composite capsules were prepared from commercial bentonite and chitosan. They were investigated in terms of their efficiency for the adsorption of toxic Cr(VI) after preparing them as a composite adsorbent. In this regard, the effects of metal concentration, adsorbent dosage, pH, temperature and contact time were investigated for the removal of Cr(VI) by using BC. For the evaluation of experimental data, Langmuir, Freundlich, Scatchard and Dubinin-Radushkevich (D-R) adsorption isotherm models were investigated and used for the adsorption equilibrium analysis of bentonite clay and BC for Cr(VI). The adsorption capacity of Cr (VI) with BC (from Scatchard isotherm) was calculated quite high.

## 2. EXPERIMENTAL

### 2.1. Materials

Bentonite (Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>·H<sub>2</sub>O, 180.1 g/mol), chitosan (medium molecular weight), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and NaOH were purchased from Sigma–Aldrich. Glutaraldehyde solution (GA) (25% in water, v:v), acetic acid and HCl were obtained from Merck. Methanol, on the other hand, was supplied from AnalaR Normapur. All the chemicals used in the experiments were of analytical grade and distilled water was used to prepare the required solutions.

### 2.2. Apparatus

In the adsorption experiments, GFL 3033 model shaker was used to mix the solutions. The Orion 900S2 model pH meter with internal reference electrodes and glass electrodes was used for pH measurements of solutions. The UV-Visible Spectrophotometer (Shimadzu UV-1700) was used for the determination of Cr(VI) in solutions. FTIR spectrum analysis was performed with Bruker VERTEX 70 FT-IR spectrometer. Microstructure of the Bentonite and BC was examined using of scanning electron microscope (SEM, ZEISS evo LS10).

### 2.3. Preparation of bentonite-chitosan composites

In 50 mL of 2% acetic acid, 1 g of chitosan was dissolved. 0.5 g of bentonite was added to the chitosan solution. The mixture was stirred for two hours to get a homogeneous mixture and then, the mixture was placed in a burette. This mixture was dropped into a coagulation solution (100 ml deionized water, 30 g NaOH, 150 ml methanol) [23]. chitosan-coated Bentonite clay composite capsules were kept in this solution overnight. After that, the composite capsules were removed from its solution via filtering. Until neutralization, the composite capsules were washed with deionized water. Then, the composite capsules were transferred to cross linking solution including 0.3 ml GA and 30 ml methanol. This mixture was refluxed 6 hours at 70°C. At the end, these composite capsules were washed with more ethanol and deionized water in order to remove excess and unreacted glutaraldehyde molecules. Finally, they were dried at room temperature. These composite capsules were analyzed for characterization and then used for Cr(VI) removal to understand their performance in adsorption process under different experimental conditions.

### 2.4. Characterization of Bentonite-chitosan composite

#### FTIR (Fourier Transform Infrared) spectroscopy

FTIR spectra of raw bentonite, chitosan-coated bentonite clay composite capsules and Cr(VI)-loaded composite capsules were taken in range of 4000–400 cm<sup>-1</sup> with Bruker Vertex FTIR Spectrum Photometer (4 cm resolution).

#### Scanning Electron Microscope/Energy Dispersive X-Ray (SEM/EDX)

Surface characterization of raw bentonite, chitosan-coated Bentonite clay composite capsules and Cr(VI)-loaded composite capsules was determined by ZEISS evo LS10 scanning electron microscope.

### 2.5. Batch Cr(VI) adsorption experiments

The stock solution of Cr(VI) was prepared by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionized water. The solution concentrations required for the adsorption study were prepared by diluting this stock solution of Cr(VI). The pH of the prepared solutions was adjusted to the wanted values by using 0.1 mol/L NaOH and 0.1 mol/L HCl solutions. pH measurements were carried out via Orion 900 S2 pH meter. Chitosan-coated Bentonite clay composite capsules (0.04 g) were added to Cr(VI) solution (58 ppm-10 ml Cr(VI), pH 2). Adsorbent-adsorbate interaction was performed with a mechanic stirrer at 200 rpm for 1 hours. After adsorption process, the amount of Cr(VI) remaining in the solution filtered with Whatman filter paper was determined with UV-Visible spectrophotometer (Shimadzu UV-1700).at 540 nm using the 1,5 diphenyl carbazide reagent [30, 31]. The amount of Cr(VI) removed by per g adsorbent was calculated using the following equation. ( $q_e$ ):

$$q_e = (C_i - C_e)V/W \quad (1)$$

where  $q_e$  is the metal-sorption capacity of the adsorbent (mg.g<sup>-1</sup>);  $C_e$  and  $C_i$  are equilibrium concentrations and the initial of Cr(VI) ion, respectively; and  $W$  is the amount of adsorbent (g)  $V$  is the volume of solution (L) [32]. The effects of adsorbent dosage (0.01-0.1 g), contact time (0-240 minutes), initial Cr(VI) concentration (10-260 ppm), pH of Cr(VI) solution (2-7) and temperature (25, 35, 45 and 55 °C) on the adsorption of Cr(VI) with the BC were investigated. These parameters were examined and the optimum conditions were found for Cr(VI) adsorption with BC. % adsorption at equilibrium was calculated by an equilibrium written as follows:

$$\text{Adsorption}(\%) = [(C_i - C_e)/C_i] \times 100 \quad (2)$$

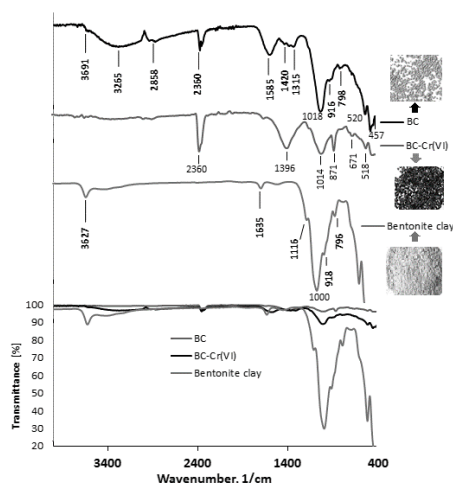
## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of bentonite, chitosan-coated Bentonite clay composite capsules (BC) and BC-Cr(VI)

#### FTIR analysis (Fourier Transform Infrared) spectroscopy

For the characterization of the adsorbents, FTIR spectra of bentonite clay, chitosan-coated Bentonite clay composite capsules (BC) and BC-Cr(VI) were taken in the range of 4000–500 cm<sup>-1</sup> wavenumber and are showed in Figure 1. When the spectra were investigated, it was observed that characteristic vibration bands were found for bentonite at 3637 cm<sup>-1</sup> (-OH stretching), 1635 cm<sup>-1</sup> (H-O-H bending), 1116 and 1000 cm<sup>-1</sup> (Si-O stretching), 918 cm<sup>-1</sup> (Al-OH stretching), 796 cm<sup>-1</sup> ((Al, Mg)-OH stretching), 648 cm<sup>-1</sup> (Al-OH bending), 518 cm<sup>-1</sup> (vibration bands belonging to Si-O bending) wavenumber. Vibration bands of BC (chitosan-coated Bentonite clay composite capsules), on the other hand, were observed at 3691 cm<sup>-1</sup> (band because of overlapping of N-H and O-H stretching bands), 3291 cm<sup>-1</sup> (a wide O-H band), 2870 cm<sup>-1</sup> (aliphatic C-H stretching), 2360 cm<sup>-1</sup> (C=C stretching), 1585 cm<sup>-1</sup> (N-H bending), 1420 and 1315 cm<sup>-1</sup> (C-N stretching), 1018 cm<sup>-1</sup> (vibration bands of C-O stretching) wavenumbers, 916 cm<sup>-1</sup> (Al-OH stretching), 798 cm<sup>-1</sup> ((Al, Mg)-OH stretching), 520 cm<sup>-1</sup> (vibration bands belonging to Si-O bending). The spectrum of BC composite indicated the combination of characteristic groups found in chitosan and bentonite [19]. After Cr(VI) adsorption of BC composite (BC-Cr(VI)), it was observed that the intensity of some bands decreased and some bands shifted. The N-H, O-H stretching band was seen at 3691 cm<sup>-1</sup> for BC shifted to 3627 cm<sup>-1</sup> and its intensity decreased; a wide O-H band at 3265 cm<sup>-1</sup> of intensity decreased, the bands belonging to C-H vibration between 2858 cm<sup>-1</sup> shifted to 2870 cm<sup>-1</sup> as well as its intensity decreased; N-H bending vibration band at 1585 cm<sup>-1</sup> shifted to 1647 cm<sup>-1</sup> and its intensity decreased. The band of C-N bending bands at 1420 and 1315 cm<sup>-1</sup> shifted to 1396 cm<sup>-1</sup> and its intensity increased; C-O stretching band at 1018 cm<sup>-1</sup> shifted to 1014 cm<sup>-1</sup> its intensity decreased; the Al-OH stretching band at 916 cm<sup>-1</sup> shifted to 871 cm<sup>-1</sup>; the intensity of the (Al, Mg)-OH stretching band at 798 cm<sup>-1</sup> decreased; and the vibration band belonging to Si-O bending band at 520 cm<sup>-1</sup> shifted to 518 cm<sup>-1</sup> [18, 24]. Figure 1 indicated that BC composite capsules had many functional groups (Si-OH, Al-OH, N-H, C-O, O-H, etc.). These functional groups are important for the adsorption of Cr(VI). As stated in prior studies in literature, the transfer of chitosan onto the bentonite and penetration of chitosan to the clay matrix were supplied via the physical and chemical interactions between bentonite and chitosan. FTIR results indicated that

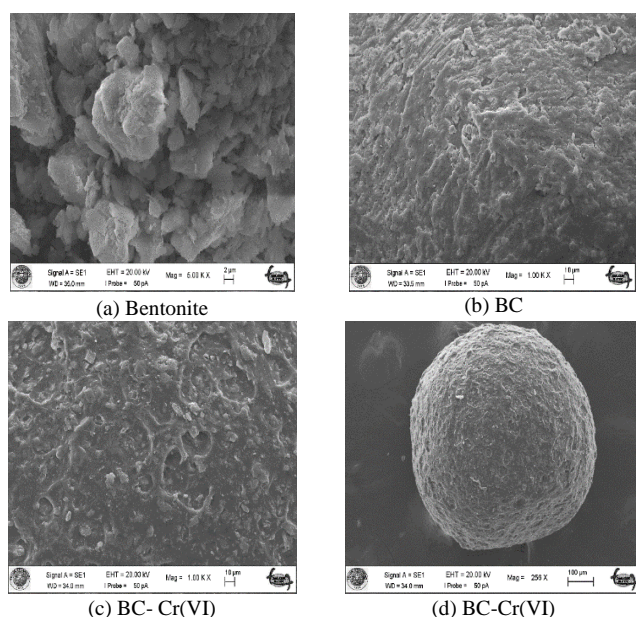
BC might be an effective adsorbent for the adsorption of Cr(VI). Bands of BC; it consists of a mixture of bands on chitosan and bentonite. [18, 19, 26, 33].



**Figure 1.** FTIR spectrum of Bentonite clay (blue), chitosan-coated Bentonite clay composite capsules (BC-red) and chitosan-coated Bentonite clay composite capsules-Cr(VI) (BC-Cr(VI)-black).

### Surface morphology

Microstructure of the Bentonite and BC was examined using of scanning electron microscope (SEM, ZEISS evo LS10). Samples were covered with gold to perform SEM analysis. The SEM of bentonite (a), BC (b) and BC-Cr(VI) are shown Figure 2. According to the results of SEM analysis, it was indicated that chitosan-coated Bentonite clay composite capsules were successfully synthesized and the pollution caused by Cr(VI) ions was removed by using these composite capsules. After chitosan-coated Bentonite clay composite capsules were formed, the changes in the shape of bentonite particles can be seen at Figure 2. It was also determined that the composite capsules were sphere in shape and the average particle size of them was lower than 100 micrometer. The surface change in the SEM micrographs demonstrated the structure of the adsorbent after and before Cr(VI) adsorption. The structure of BC-composite capsules is observed as rough and folded. After the adsorption of Cr(VI), the surfaces of the BC capsules had a very smooth surface. This smooth structure showed that the surface filled and that Cr(VI) ions were adsorbed on the BC surface.



**Figure 2.** SEM micrograph of Bentonite clay (a), chitosan-coated Bentonite clay composite capsules (BC-b) and chitosan-coated Bentonite clay composite capsules-Cr(VI) (BC-Cr(VI)-c, d).

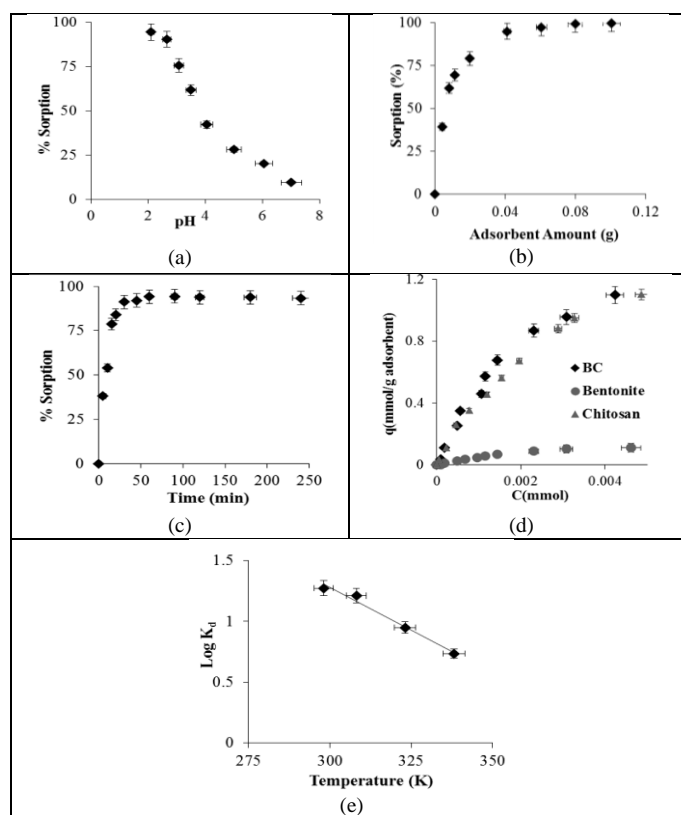
## 3.2. Adsorption performances of Cr(VI) ion with chitosan-coated Bentonite clay composite capsules (BC)

### 3.2.1. Effect of pH

pH is one of the important parameters in the adsorption because it affects the surface mechanism of the adsorbent, in other words, to the binding points of pollutant and the adsorbent. pH value of the solution affects the surface charge of the adsorbent, the degree of ionization and the adsorbed species.

Moreover, adsorption degree also changes depending on the pH value since the concentration of dissolved species will change because of precipitation and hydrolysis of metal ions. Since there is a competition between metal ions and hydrogen ions for active areas on the surface of the adsorbent, the pH of the media greatly influences metal binding. Therefore, the effect of pH on the adsorption of Cr(VI) was the first study and the results was given in Figure 3a.

As it can be seen in Figure 3a, at pH 2.1, while 58 ppm Cr(VI) ion was removed with 95%, this rate decreased to 28% at pH=5. There is an inverse proportion between Cr(VI) removal and pH values. As the pH decreased, the amount of Cr(VI) adsorbed by BC was observed to be increased. This situation can be attributed the cationic structure of the adsorbent and to the presence of excess OH<sup>-</sup> ions in the solution. Since the initial pH value of the solution both affects metal binding sites and water chemistry, it is necessary to determine optimum pH correctly to evaluate the efficiency of adsorption process [11]. The optimum pH of the Cr(VI) adsorption with the BC composite adsorbent was found to be approximately 2.



**Figure 3.** (a) Effect of pH on the removal of Cr(VI) using BC (adsorbent amount: 4 g/L, initial concentration of Cr(VI): 58 ppm, temperature:  $25 \pm 1$  °C, and contact time: 60 min for BC). (b) Effect of adsorbent dosage on removal of Cr(VI) using BC (initial concentration of Cr(VI): 58 ppm, initial solution pH: 2, contact time: 60 min, and temperature:  $25 \pm 1$  °C for BC). (c) Effect of contact time on removal of Cr(VI) with BC (initial concentration of Cr(VI): 58 ppm, initial solution pH: 2, adsorbent amount 4 g/L, and temperature  $25 \pm 1$  °C for BC). (d) Adsorption isotherms of Bentonite clay, Chitosan and BC (solution pH: 2, adsorbent amount: 4 g/L, contact time: 60 min, and temperature:  $25 \pm 1$  °C for BC). (e) Effect of temperature on the adsorption of Cr(VI) by BC (initial concentration of Cr(VI): 58 ppm, adsorbent amount: 4 g/L, contact time: 60 min, and solution pH: 2 for BC).

### 3.2.2. Adsorbent Dosage

In terms of both the efficiency and cost of the process, it is of great importance to determine the appropriate adsorbent dosage in the adsorption processes. Moreover, the amounts of functional groups present on the surface binding points of the adsorbent have an important role for the removal of target metals. In this part of the study, a series of experiments were performed with 58 ppm Cr(VI) solution in varying adsorbent dosages (0.01-0.1 g) and as a result, the effect of adsorbent amount on Cr(VI) adsorption was investigated.

When the graph given in Fig. 3b was investigated, it was observed that as the adsorbent dosage increased, the sorption rate of metal removal also increased. While Cr(VI) removal was 69% with 0.01 g adsorbent, it increased to 94.95% as the adsorbent dosage was increased to 0.04 g. When the amount of adsorbent was 0.1 g, the % sorption value was 99.84%. After plateau value, the increase in the amount of BC does not significantly affect the Cr(VI) adsorption. Since the increase in sorption decreased after 0.04 g adsorbent amount, the optimum amount of adsorbent was taken as 0.04 g. After this point; since the adsorption event was an equilibrium event, the effect of increasing the amount of BC upon removal of Cr(VI) was not high. At the beginning, the increased adsorption percentage of Cr(VI) ions could be attributed to the increased availability of adsorption sites along with an increase in the amount of BC. In balance, the percentage of Cr(VI) adsorption probably remained constant due to saturation of surface areas in the adsorbent. Since the surface area increased as increasing the adsorbent dosage, the amount of adsorbed Cr(VI) per unit mass of adsorbent also increased. Since adsorption is a surface phenomenon, the efficiency and intensity of adsorption process is directly proportional to surface area. Similar results were obtained in the literature [2, 35, 36].

### 3.2.3. Effect of Contact Time On Cr(VI) Removal

In order to mention the efficiency of the process, contact time is another important parameter that should be investigated in adsorption. In this study, metal removal percentages were calculated in terms of contact time while all other parameters were kept constant. 0.04 g adsorbent was mixed with 58 ppm Cr(VI) solution at pH 2 at varying time intervals and sorption percentage was drawn against contact time (Figure 3c). When the graph was investigated, adsorbed metal amount rapid increased within a contact time of 0- 60 minutes, however, a significant difference was not observed for the measurements after 60 minutes. As it can be seen in Figure 3c, because of Cr(VI) ions adsorbed on the outer surface of the adsorbent, initial adsorption rate was higher. At initial stage, since adsorbent had a wide surface area for the adsorption of metal ions and adsorbent centers were free, metals ions easily interact with these centers and therefore the adsorption was faster. As the adsorption centers on the surface were occupied, metal ions were transferred from outer surface of the adsorbent to the inner surface, metal removal rate was got under control and adsorption process reached an equilibrium. Slow adsorption after initial period might be due to slower diffusion of solution through the adsorbent [37, 38].

### 3.2.4. Effect of Initial Cr(VI) Concentration On the Adsorption Process

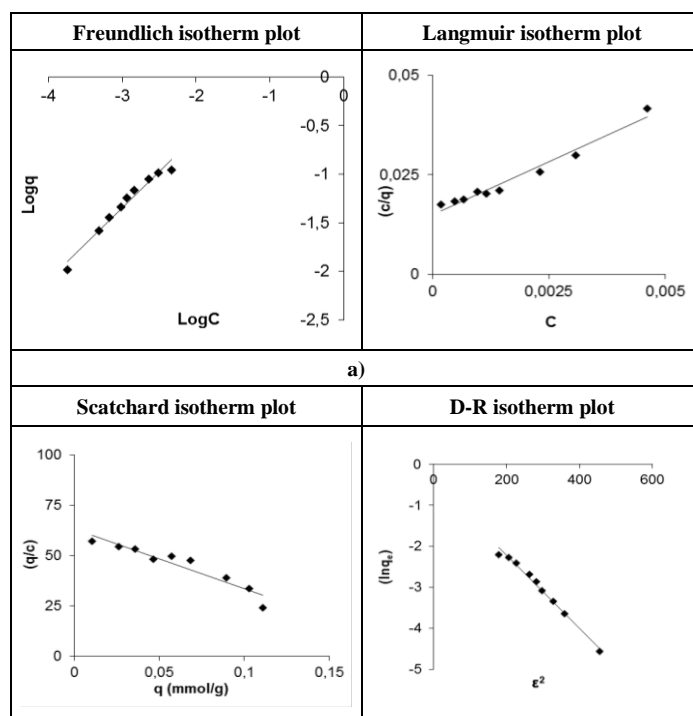
In this part of the study carried out with different initial concentrations, the relationship between equilibrium concentrations obtained and amount of adsorbed metal ion per unit mass of adsorbent was investigated and isotherm data were calculated by drawing adsorption isotherms. The effect initial Cr(VI) concentration on removal of Cr(VI) (10-260 mg/L concentration range,  $25 \pm 1$  °C, initial solution pH 2, adsorbent amount 25 g/L; 4 g/L for bentonite clay and BC respectively) with bentonite and BC is shown in Figure 3d. For the determination of suitability of these data to the isotherm models, it is necessary to present the relationship between equilibrium concentration ( $C_e$ ) and  $C_e/q_e$ . This was explained with the equations given in Table 1, then the isotherm constants were calculated with the slopes of the curves and the y-intercept of the equations. In these equations,  $C_e$  indicated metal concentration at equilibrium (mg/L);  $\frac{x}{m} = q_e$  was the amount of adsorbed metal ion by the adsorbent (mg/g) [28, 39-41].

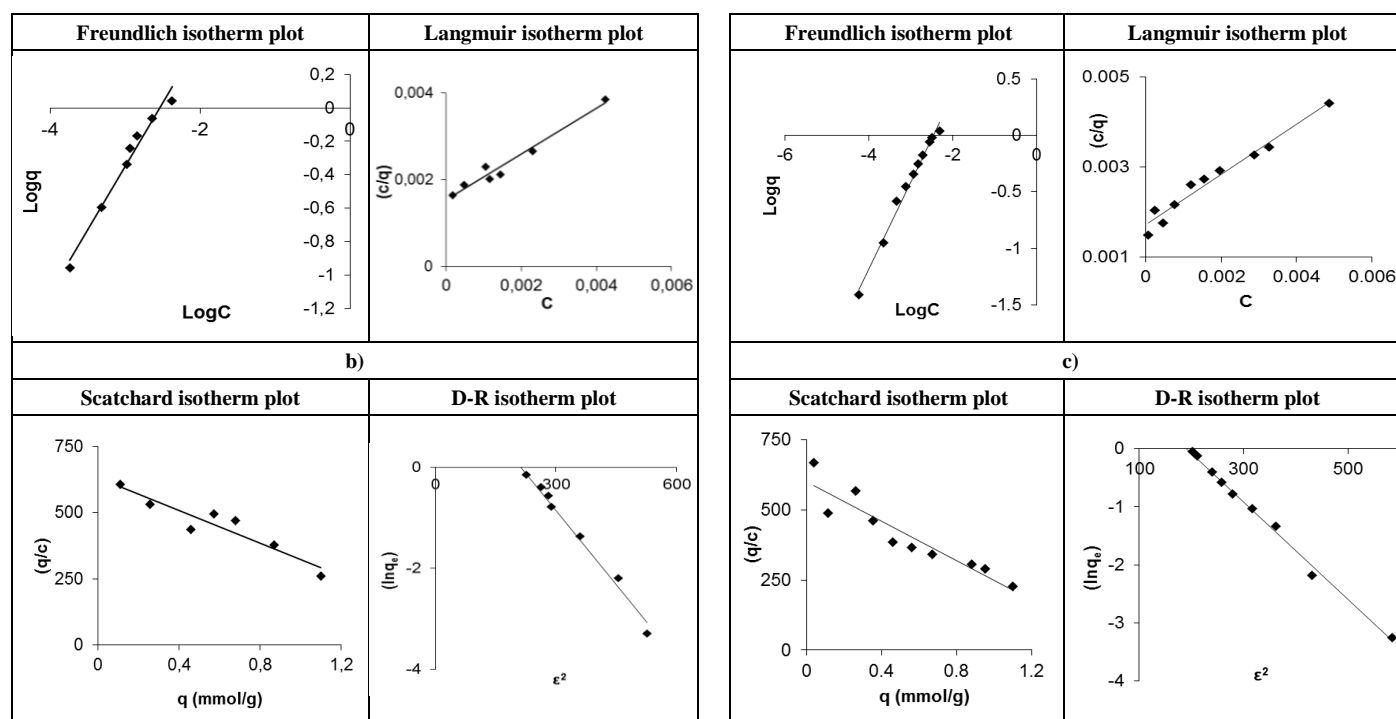
In Table 1, the constants of Langmuir, Freundlich, Scatchard and Dubinin-Radushkevich (D-R) isotherms are given. Table 1 shows the results of the modified Langmuir, Freundlich, Scatchard and D-R isotherms analysis for the adsorption of Cr(VI) on the bentonite clay, chitosan and BC from aqueous solutions. The equilibrium relationships between the adsorbent and Cr(VI) are explained by adsorption isotherms. Correlation coefficients ( $R^2$  value) calculated

from modified Langmuir, Freundlich, Scatchard, and D-R isotherms models. When all isotherms were compared,  $R^2$  values were close to each other. (Figure 4a, b). Therefore, it is thought to have more than one adsorption mechanism. The parameters of the isotherms showed respectively for bentonite clay, chitosan and BC in Figure 4a, b are given in Table 1. For Freundlich isotherm,  $k$  and  $n$  are constant values. For Langmuir isotherm,  $A_s$  is the adsorption capacity (mg/g adsorbent),  $K_b$  is a constant related with adsorption energy [28, 32, 35]. In Scatchard isotherm,  $Q_s$  is the adsorption capacity (mg/g adsorbent),  $K_s$  is the binding constant [2]. In Dubinin Radushkevich (D-R) isotherm,  $E$  indicates adsorption energy ( $\text{kJ mol}^{-1}$ ) and  $K$  refers to adsorption energy constant [32, 42, 43].

It is possible with D-R isotherm to calculate adsorption energy ( $E_{ad}$ ; kJ/mol) which gives information about physical and chemical characteristics of adsorption. If adsorption energy is  $E_{ad} < 8$  kJ/mol, adsorption process is physical adsorption; if  $E_{ad}$  is between 8-16 kJ/mol, ion exchange or complex formation and if  $E_{ad} > 16$ , then particle diffusion are dominant. For Cr(VI) adsorption with chitosan and BC,  $E_{ad}$  were found as 8.84 and 8.006 kJ/mol respectively which indicated that ion exchange and complex formation were dominating the adsorption process.  $E_{ad}$  was calculated as 7.495 kJ/mol in Cr(VI) adsorption with bentonite clay. Physical adsorption is dominant in Cr(VI) adsorption process with bentonite clay. It was resulted that Scatchard isotherm was more suitable for this removal process by BC adsorbent with the calculated correlation coefficients. Scatchard isotherm assumes that adsorption potential was constant and the surface of the particle was homogeneous. According to this isotherm, maximum adsorption capacity of BC for Cr(VI) removal was calculated as 106.444 mg/g and it was determined that this capacity was higher than other adsorbents which were used in previous studies in the literature. Maximum Cr(VI) adsorption capacity of bentonite clay and chitosan was found as 11.076 and 88.705 mg/g, respectively.

The maximum Cr(VI) adsorption capacity of BC is approximately 10 times the capacity of bentonite clay. Cr(VI) adsorption process with bentonite clay is slower and requires longer durations. The maximum adsorption capacity of the Cr(VI) ion of the bentonite clay is also low. The adsorption process with BC is completed shortly and the maximum adsorption capacity is obtained higher as seen in Table 1. This results showed that the interest of Cr(VI) to the BC composite capsule was quite high. Many investigations have been carried out related to removal of Cr(VI) from the aqueous solution with the adsorption and Cr(VI) adsorption capacities of these studies are given in Table 2. When compared with the other adsorbents in the literature, it has been found that the BC composite adsorbent has a considerably high capacity for the removal of Cr(VI).





**Figure 4.** Langmuir, Freundlich, Dubinin-Radushkevich and Scatchard isotherms plot for the adsorption of Cr(VI) onto (a) Bentonite clay, (b) chitosan-coated Bentonite clay composite capsules (BC) and Chitosan.

**Table 1.** Isotherm, kinetic and thermodynamic data for removal of Cr(VI) using Bentonite clay and chitosan-coated Bentonite clay composite capsules (BC).

Isotherm Model	Linear Equations	Curve	Parameters	Bentonite	Chitosan	BC
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{A_s K_b}$	$(C_e/q_e)$ vs. $C_e$	$A_s$	9.770	93.385	98.620
			$K_b$	354.790	327.53	351.530
			$R^2$	0.9671	0.963	0.9650
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	$k$	8.100	80.720	83.580
			$n$	1.330	1.294	1.320
			$R^2$	0.968	0.988	0.976
Scatchard	$\left(\frac{q_e}{C_e}\right) = Q_s K_s - q_e K_s$	$q_e$ vs. $q_e/C_e$	$K_s$	297.160	351.9	308.820
			$Q_s$	11.076	88.705	106.444
			$R^2$	0.935	0.8686	0.983
Dubinin Radushkevich (D-R)	$\ln q_e = \ln X_m - K \epsilon^2$ $\epsilon: RT \ln \left(1 + \frac{1}{C_e}\right)$ $\epsilon$ : Polanyi potential $E_{ad} = (2K_1)^{-\frac{1}{2}}$ $E_{ad}$ = Adsorption Energy	$\epsilon^2$ vs. $\ln q_e$	$K$	0.0089	0.064	0.0078
			$E_{ad}$	7.495	8.840	8.006
			$R^2$	0.988	0.991	0.984
Thermodynamic parameters	$\Delta G = \Delta H - T \Delta S$		$\Delta H^\circ$ (J/mol)		0.270	
			$\Delta S^\circ$ (J/K · mol)		105.500	
			$\Delta G^\circ$ (J/mol)	T = 298 K	-30927.14	
				T = 308 K	-32509.64	
		T = 318 K	-34092.15			
		T = 328 K	-35674.65			

**Table 2.** Comparative of the adsorption capacities of Cr(VI) ions onto the different adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Turkish perlite with $\alpha$ -MnO <sub>2</sub> (PAM)	7.6 0	[2]
Turkish perlite $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (PGI)	8.64	[2]
Ti-Fe kaolinite composite	23.47	[4]
Chestnut oak shells	4.44	[7]
Prepared carbon with chestnut shells	33.00	[7]
Smectite Natural clay	12.50	[13]
Activated Smectite Natural clay with sulfuric acid	19.23	[13]
Acid-treated sawdust composite beads (SDCCB)	122.30	[17]
Cross-Linked Magnetic Chitosan Beads	69.40	[18]
Chitosan/Zeolite film	17.28	[18]
Chitosan	35.60	[18]
N-2-hydroxypropyl trimethyl ammonium chloride chitosan-bentonite	22.17	[18]
Cross-linked chitosan	50.00	[18]
Oak wood charcoal	30.10	[19]
Cross-linked chitosan/bentonite (obtained from China) composite (CCB)	89.13	[19]
Oak wood charcoal ash	46.17	[19]
Mesoporous NiO nanoparticles	4.73	[19]
KIP 210 resin	100.00	[19]
Ammonium sulfamate-bacterial cellulose	22.30	[19]
Tannin-immobilized activated clay	24.09	[19]
Cross-linked chitosan/bentonite composite	89.13	[19]
Chitosan(Chitosan extracted from this waste prawn shell)-modified Bijoypur clay biocomposite (CHT-MC)	73.00	[21]
Raw kaolinite	11.60	[22]
Kaolinite activated by acid	13.90	[22]
Kaolinite activated by ZrO	10.90	[22]
Kaolinite activated by BA(Tetrabutylammonium)	10.60	[22]
Bentonite-nZVI (Nanoscale zero-valent iron) nano-composite	66.10	[22]
Mt-algi/PA (Alginate-montmorillonite/polyaniline)	29.89	[22]
Mt(Montmorillonite)/Cellulose and Sodium	22.20	[22]
Bentonite/Acid activated pillared	1030	[22]
N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC)-bentonite nanocomposite	22.17	[25]
Commercial Activated carbon (CAC).	15.47	[25]
Commercial bentonite	11.076	In this study
Chitosan	88.705	In this study
BC	106.44	In this study

### 3.2.5. Thermodynamic analysis

Adsorption of Cr(VI) onto BC has definitely carried out different temperatures (25 °C, 35 °C, 45 °C, and 55 °C) for thermodynamic analysis (Figure 3e). The thermodynamic parameters including  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the adsorption of Cr(VI) are calculated from plotted data, and the results are given in Table 1. The effect of temperature on the adsorption of Cr(VI) ions was investigated and the adsorption capacity was calculated as higher at low temperatures for BC composite capsules. By using Van't Hoff equation, a graph of  $\log K_c$  vs.  $1/T$  was drawn, standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes were calculated [40].

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\Delta G^\circ = \Delta G^\circ + T\Delta S^\circ \quad (4)$$

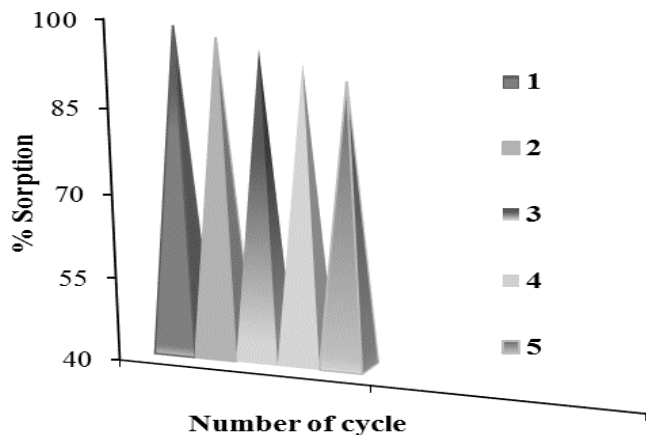
$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (\text{Van't Hoff equation}) \quad (5)$$

( $\Delta S^\circ$ ) and ( $\Delta H^\circ$ ) values were found from the y-intercept ( $\Delta S^\circ/2.303R$ ) and the slope of the curve ( $\Delta H^\circ/2.303R$ ), respectively. Thermodynamic analysis (Table 1) indicated that adsorption with BC composite capsules for the removal of Cr(VI) ions was endothermic in nature. At the same time, the adsorption energy of this process was found as 8-16 kJ mol<sup>-1</sup> in D-R isotherm for the adsorption of Cr(VI) by BC.

The positive value of enthalpy and the results of D-R isotherm indicated that mechanisms such as ion exchange, electrostatic interaction and complexation were dominant for Cr(VI) adsorption with BC. Moreover, the negative value of Gibb's free energy for Cr(VI) adsorption by BC indicated that Cr(VI) removal process was spontaneous.  $\Delta S^\circ$  value for Cr(VI) adsorption was also found positive. Positive  $\Delta S^\circ$  value referred to an increase in entropy in the solid-liquid interface throughout the adsorption process. According to these thermodynamic results, it was resulted that adsorption of Cr(VI) ions by BC composite capsules was a spontaneous reaction. Similar results were obtained in some studies in the literature [30, 44-47].

### 3.3. Desorption studies

Desorption studies are important to economic point of view and to assess the reusability of BC composite capsules as a promising adsorbent for waste water treatment. To remove the adsorbed Cr (VI) ions on the BC surface, 0.1 M NaOH solution was used. After the adsorption equilibrium study, 20 mL of 0.1 M NaOH solution was added to 1 g Cr (VI) adsorbed BC and the mixture was stirred continuously at room temperature for 60 minutes. Then the adsorbent was treated with 1M HCl. To remove NaOH and HCl contamination on the surface of the adsorbent, regenerated BC was washed several times with MilliQ water. Then, the regenerated BC was reused at pH 2.1 for 5 adsorption cycles. Therefore, it has been concluded that the BC composite adsorbent has excellent recycle ability to remove Cr(VI) from the aqueous solution. The results are shown in Figure 5.



**Figure 5.** Adsorption-desorption cycles for Cr(VI) with BC composite adsorbent.

### CONCLUSIONS

As a result of this study, efficient results were calculated for the removal of Cr(VI) by BC composite. When compared to other adsorbents obtained from natural materials in the literature, the usage of this composite capsule has a potential for large-scale adsorption processes under the required optimization conditions. As a conclusion, maximum removal was obtained at pH 2. Optimum adsorbent dosage was determined as 0.04 g for Cr(VI) adsorption on BC. At the same time, as the initial concentration was increased, the removal rate of Cr(VI) decreased. The obtained results of isotherm models indicated that the experimental data were well fitted to Scatchard adsorption isotherm and the adsorption capacity was calculated from this isotherm model. While the maximum adsorption capacity of the raw bentonite clay for removal Cr(VI) was calculated as 11.076 mg/g, the adsorption capacity of chitosan-coated Bentonite clay composite capsules (BC) for the removal of Cr(VI) was found as 106.444 mg/g which is a quite high value. According to thermodynamic results, while positive  $\Delta H^\circ$  value indicated that adsorption was endothermic, positive  $\Delta S^\circ$  value indicated that entropy increased in adsorption process and the reaction was induced. Negative values of standard free energy showed that the process was spontaneous. Both thermodynamic results and the adsorption energy value found by D-R isotherm ( $E=8.06$  kJ/mol) resulted that mechanisms such as ion exchange, electrostatic interaction and complexation were dominant for Cr(VI) adsorption on BC. These findings proved that obtaining different composites by using different clays and chitosan might result in materials which have different chemical composition and different surface morphology which are more effective. As a conclusion, heavy metal as well as dyes and other pollutants can be removed by these composite materials in higher removal efficiencies.

### CONFLICT OF INTEREST

The author declares no conflict of interest.

### ACKNOWLEDGMENT

I would like to thank Associate Professor Serpil Edebali for her support in preparing this study.

### REFERENCES

- Mudzielwana, R., Gitari, M. W., Akinyemi, S. A., & Msagati, T. A. M. Performance of Mn 2+-modified bentonite clay for the removal of fluoride from aqueous solution. *South African Journal of Chemistry*, 71(1), 15. (2018)
- Edebali, S. Alternative Composite Nanosorbents Based on Turkish Perlite for the Removal of Cr(VI) from Aqueous Solution. *Journal of Nanomaterials*, 2015. (2015)
- Auta, M., & Hameed, B. H. Chitosan-clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. *Chemical Engineering Journal*, 237, 352. (2014)
- Fida, H., Guo, S., & Zhang, G. Preparation and characterization of bifunctional Ti-Fe kaolinite composite for Cr(VI) removal. *Journal of Colloid and Interface Science*. (2015)
- Uddin, M. K. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*. (2017)
- Ghomri, F., Lahsini, A., Laajeb, A., & Addaou, A. The removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. *LARHYSS Journal ISSN 1112-3680*, (12). (2013)
- Niazi, L., Lashanizadegan, A., & Shariffard, H. Chestnut oak shells activated carbon: Preparation, characterization and application for Cr (VI) removal from dilute aqueous solutions. *Journal of Cleaner Production*. (2018)
- Gupta, V. K., Chandra, R., Tyagi, I., & Verma, M. Removal of hexavalent chromium ions using CuO nanoparticles for water purification applications. *Journal of Colloid and Interface Science*. (2016)
- Yang, J., Yu, M., & Chen, W. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from longan seed: Kinetics, equilibrium and thermodynamics. *Journal of Industrial and Engineering Chemistry*. (2015)
- Ghaneian, M. T., Bhatnagar, A., Ehrampoush, M. H., Amrollahi, M., Jamshidi, B., Dehvari, M., & Taghavi, M. Biosorption of hexavalent chromium from aqueous solution onto pomegranate seeds: kinetic modeling studies. *International Journal of Environmental Science and Technology*. (2017)
- Qi, W., Zhao, Y., Zheng, X., Ji, M., & Zhang, Z. Adsorption behavior and mechanism of Cr(VI) using Sakura waste from aqueous solution. *Applied Surface Science*. (2016)
- Nasseh, N., Taghavi, L., Barikbin, B., & Khodadadi, M. Advantage of almond green hull over its resultant ash for chromium(VI) removal from aqueous solutions. *International Journal of Environmental Science and Technology*. (2017)
- Khalfa, L., Cervera, M. L., Bagane, M., & Souissi-Najar, S. Modeling of equilibrium isotherms and kinetic studies of Cr (VI) adsorption into natural and acid-activated clays. *Arabian Journal of Geosciences*, 9(1), 75. (2016)
- Rathnayake, S. I., Martens, W. N., Xi, Y., Frost, R. L., & Ayoko, G. A. Remediation of Cr (VI) by inorganic-organic clay. *Journal of Colloid and Interface Science*. (2017)
- Qiu, W., Yang, D., Xu, J., Hong, B., Jin, H., Jin, D., Wang, X. Efficient removal of Cr (VI) by magnetically separable CoFe<sub>2</sub>O<sub>4</sub>/activated carbon composite. *Journal of Alloys and Compounds*, 678, 179. (2016)
- Vunain, E., Mishra, A. K., & Mamba, B. B. Dendrimers, mesoporous silicas and chitosan-based nanosorbents for the removal of heavy-metal ions: A review. *International Journal of Biological Macromolecules*. (2016)
- Alhaji, N. M. I., & Begum, K. M. T. M. Optimization and Kinetic Study for the Removal of Chromium (VI) Ions by Acid Treated Sawdust Chitosan Composite Beads. *International Research Journal of Pure and Applied Chemistry*, 5(2), 160. (2015)
- Moussout, H., Ahlafi, H., Aazza, M., & El Akili, C. Performances of local chitosan and its nanocomposite 5%Bentonite/Chitosan in the removal of chromium ions (Cr(VI)) from wastewater. *International Journal of Biological Macromolecules*, 108, 1063. (2018)
- Liu, Q., Yang, B., Zhang, L., & Huang, R. Adsorptive removal of Cr(VI) from aqueous solutions by cross-linked chitosan/bentonite composite. *Korean Journal of Chemical Engineering*, 32(7), 1314. (2015)
- Chen, L., Wu, P., Chen, M., Lai, X., Ahmed, Z., Zhu, N., ... Liu, T. Preparation and characterization of the eco-friendly chitosan/vermiculite biocomposite with excellent removal capacity for cadmium and lead. *Applied Clay Science*. (2018)
- Biswas, S., Islam, M. M., Hasan, M. M., Rimu, S. H., Khan, M. N., Haque, P., & Rahman, M. M. Evaluation of Cr (VI) Ion Removal from Aqueous Solution by Bio-Inspired Chitosan-Clay Composite: Kinetics and Isotherms. *Iranian Journal of Chemical Engineering*, 15(4). (2018)
- Yadav, V. B., Gadi, R., & Kalra, S. Clay based nanocomposites for removal of heavy metals from water: A review. *Journal of environmental management*, 232, 803. (2019)

23. Sargin, I., Kaya, M., Arslan, G., Baran, T., & Ceter, T. Preparation and characterisation of biodegradable pollen-chitosan microcapsules and its application in heavy metal removal. *Bioresource Technology*, 177, 1. (2015)
24. Moussout, H., Ahlafi, H., Aazza, M., & Amechrouq, A. Bentonite/chitosan nanocomposite: preparation, characterization and kinetic study of its thermal degradation. *Thermochimica Acta*, 659, 191. (2018)
25. Giannakas, A., & Pissanou, M. Chitosan/Bentonite Nanocomposites for Wastewater Treatment: A Review. *SF J Nanochem Nanotechnol*. 2018; 1 (1), 1010. (2018)
26. Futralan, C. M., Kan, C. C., Dalida, M. L., Hsien, K. J., Pascua, C., & Wan, M. W. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. *Carbohydrate Polymers*. (2011)
27. Waheed Thany, Z., & Mousa Ridha, A. Use of chitosan impregnated modified bentonite as an adsorbent for remediation of oil spill from aqueous solution. *International Journal of Engineering & Technology*, 7(4), 4380. (2018)
28. Zou, C., Jiang, W., Liang, J., Sun, X., & Guan, Y. Removal of Pb (II) from aqueous solutions by adsorption on magnetic bentonite. *Environmental Science and Pollution Research*, 26(2), 1315. (2019)
29. Ugwu, I. M., & Igbokwe, O. A. Sorption of Heavy Metals on Clay Minerals and Oxides: A Review. In *Advanced Sorption Process Applications*. IntechOpen. (2019)
30. Altun, T., Parlayıcı, Ş., & Pehlivan, E. Hexavalent chromium removal using agricultural waste "rye husk". *Desalination and Water Treatment*. (2016)
31. Melo, J. S., & D'Souza, S. F. Removal of chromium by mucilaginous seeds of *Ocimum basilicum*. *Bioresource Technology*. (2004)
32. Matouq, M., Jildeh, N., Qtaishat, M., Hindiyeh, M., & Al Syouf, M. Q. The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods. *Journal of Environmental Chemical Engineering*. (2015)
33. Li, J., Cai, J., Zhong, L., Cheng, H., Wang, H., & Ma, Q. Adsorption of reactive red 136 onto chitosan/montmorillonite intercalated composite from aqueous solution. *Applied Clay Science*, 167, 9. (2019)
34. Zhao, Y., Qi, W., Chen, G., Ji, M., & Zhang, Z. Behavior of Cr(VI) removal from wastewater by adsorption onto HCl activated Akadama clay. *Journal of the Taiwan Institute of Chemical Engineers*. (2015)
35. Akram, M., Bhatti, H. N., Iqbal, M., Noreen, S., & Sadaf, S. Biocomposite efficiency for Cr(VI) adsorption: Kinetic, equilibrium and thermodynamics studies. *Journal of Environmental Chemical Engineering*. (2017)
36. Mishra, A., Dubey, A., & Shinghal, S. Biosorption of chromium(VI) from aqueous solutions using waste plant biomass. *International Journal of Environmental Science and Technology*. (2015)
37. Georgieva, V. G., Tavlieva, M. P., Genieva, S. D., & Vlaev, L. T. Adsorption kinetics of Cr(VI) ions from aqueous solutions onto black rice husk ash. *Journal of Molecular Liquids*. (2015)
38. Pandey, S., & Mishra, S. B. Organic-inorganic hybrid of chitosan/organoclay bionanocomposites for hexavalent chromium uptake. *Journal of Colloid and Interface Science*, 361(2), 509. (2011)
39. Fouodjouo, M., Fotouo-Nkaffo, H., Laminsi, S., Cassini, F. A., de Brito-Benetoli, L. O., & Debacher, N. A. Adsorption of copper (II) onto cameroonian clay modified by non-thermal plasma: Characterization, chemical equilibrium and thermodynamic studies. *Applied Clay Science*. (2017)
40. Lin, J., Wu, Y., Khayambashi, A., Wang, X., & Wei, Y. Preparation of a novel CeO<sub>2</sub>/SiO<sub>2</sub> adsorbent and its adsorption behavior for fluoride ion. *Adsorption Science and Technology*, 36(1–2), 743. (2018)
41. Ayawei, N., Ebelegi, A. N., & Wankasi, D. Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*. (2017)
42. Parlayıcı, S. Alginate-coated perlite beads for the efficient removal of methylene blue, malachite green, and methyl violet from aqueous solutions: kinetic, thermodynamic, and equilibrium studies. *Journal of Analytical Science and Technology*, 10(1), 4. (2019)
43. Chaudhry, S. A., Khan, T. A., & Ali, I. Equilibrium, kinetic and thermodynamic studies of Cr(VI) adsorption from aqueous solution onto manganese oxide coated sand grain (MOCSG). *Journal of Molecular Liquids*. (2017)
44. Liu, X., & Lee, D. Thermodynamic parameters for adsorption equilibrium of heavy metals and dyes from wastewaters. *Bioresource Technology*, 160, 24. (2014)
45. Salih, S. S., & Ghosh, T. K. Highly efficient competitive removal of Pb (II) and Ni (II) by chitosan/diatomaceous earth composite. *Journal of environmental chemical engineering*, 6(1), 435. (2018)
46. Tulun, S., Bahadir, T., Simsek, I., & Karatas, M. THE REMOVAL OF NICKEL IONS WITH WALNUT SHELL. *Turkish Journal of Engineering (TUJE)*, 3(2), 102. (2019)
47. Konicki, W., & Pelech, I. Removing Cationic Dye from Aqueous Solutions Using as-grown and Modified Multi-Walled Carbon Nanotubes. *Polish Journal of Environmental Studies*, 28(2), 717. (2018)