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# Biosorption of toxic hexavalent chromium(VI) in aqueous solution by peanut shell biomass: equilibrium and kinetic studies

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## ABSTRACT

The purpose of this study is to evaluate the possibility of using an agricultural residue which is peanut shell powder (PSP) as an adsorbent for the removal of a heavy metal that is hexavalent chromium from wastewater. Chromium(VI) adsorption is studied in batch mode and some influencing parameters were tested, such as particle size, pH variation, adsorbent dose, stirring speed and initial chromium concentration. The results obtained achieved 99% chromium(VI) removal rates under optimal conditions, for an initial chromium(VI) concentration of 10 $mg \cdot L^{-1}$. Scanning electron microscopy and Fourier-transform infrared spectroscopy were used to determine the physico-chemical characteristics of this biomaterial. The results showed that the PSP surface contains a large number of functional groups and has surface properties suitable for the biosorption of Cr(VI) ions. The experimental results obtained follow the two adsorption models of Langmuir and Freundlich, both models showed good results with correlation coefficients of 0.9695 and 0.9977, respectively. The chromium(VI) adsorption process was better represented by a second-order kinetic law ($R^2$ = 0.99). Our investigation revealed that peanut shell-based biomaterial is a good candidate for the removal of Cr(VI) from aqueous solutions.

*Keywords:* Peanut shells; Hexavalent chromium; Biosorption; Isotherm; Kinetic modeling

## 1. Introduction

It is not secret that the natural environment is facing a rapidly growing degeneration, which has inspired some research to provide solutions for environmental remediation. Previous studies have broadly shown that major pollution of natural ecosystems can be traced to anthropogenic sources, with industrial activity predominant [1]. Industrial wastewater containing heavy metals is one of the most worrisome problems for ecosystems. Hexavalent chromium is widely used in industrial fields, it can be found in various oxidation states ranging from – II to VI. Of these, only Cr(III) and Cr(VI) are stable forms in the natural environment. However, Cr(VI) is rarely naturally generated, is relatively soluble in aqueous systems and is easily transformed in groundwater [2]. Both of Cr(III) and Cr(VI) forms are known to be highly toxic by inhalation and dermally, causing lung cancer, skin irritation, asthma and nasal ulcers [3].

Metal ions are not degradable into harmless end products, such as biodegradable organic pollutants [4]. Considering its toxicity, several suitable treatment methods for the removal of hexavalent chromium from industrial waste water and groundwater resources are under development and application. The most common treatment methods are metal

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organic framework [2], precipitation [5,6], ion exchange [7,8], membrane separation (reverse osmosis and ultrafiltration) [9,10], and electrochemical reduction [1]. But most of the above treatment methods have limitations, including long treatment times, high energy consumption, toxic sludge production, high operating and maintenance costs and limited removal efficiency.

Adsorption is a method of choice, it is a widely used physicochemical method for removing heavy metals because adsorption does not require a high operating temperature and can remove multiple substances at the same time. Recently, various adsorbents have received more attention in removing metal ions [2]. The liquid–solid interface adsorption process is mainly affected by pH value of the solution, operating temperature, contact time, amount of adsorbent, initial concentration of the adsorbate, surface area of the adsorbent and the stirring speed. In order to obtain the maximum adsorption capacity, it is necessary to optimize the process variables to improve the removal efficiency of the adsorbent [11]. Currently, the most used and efficient physical method in the industry is adsorption on activated carbons. These materials occupy an important position as adsorbents and are widely used in gas and water purification [12]. However, due to the use of non-renewable and relatively expensive raw materials, such as coal, in many countries, commercially available activated carbon is still regarded as an expensive material, which is unjustified in pollution control applications [13,14] The search for an alternative to the conventional treatments for removing Cr(VI) makes it possible to use biosorption methods. Compared with conventional methods, these biosorbents exhibit characteristics such as removal efficiency, low cost and high capacity reduction in the generation of biological and chemical residues, and regeneration of biosorbents through metal recovery. Waste biomaterials are highly efficient and low-cost biosorbents [15]. Different biosorbents have been used for the adsorption of Cr(VI), such as biochar [6], bivalve mollusk shells [16], wheat shell [17], *Lantana camara* fruit [18], custard apple seeds, *Aspergillus niger* [19], *Caryota urens* seeds [20] and *Lentinus sajor-caju* [29].

The wilaya of El-Oued, in Algeria, recorded a production of 124,000 quintals of peanuts during the current agricultural season, reported the local Directorate of Agricultural Services (DSA). This production, carried out on a total area of 4,000 hectares, is up 18% compared to last year's production. The cultivation of peanuts, a plant of the Fabaceae family used in the manufacture of table oil. It would be important if we could recover the amount of waste generated by this industry and find other environmentally friendly uses. The purpose of this research is to study the adsorption capacity of peanut shell powder as an adsorbent to remove Cr(VI) from aqueous solutions. Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) are used to identify the various functional groups on the cell wall of the biosorbent and to study the surface morphology of this biomaterial. Batch experiments are conducted to examine the impact of different parameters such as the pH value of the solution, the ratio of the used biomass, the particle size, the metal concentration and the stirring speed on the biosorption of Cr(VI) from aqueous solution. In addition, the modeling of Cr(VI) adsorption is performed using adsorption isotherms and kinetic models.

## 2. Materials and methods

### 2.1. Reagents and materials

The peanut shells were obtained from the fruits harvested in El Oued, Algeria.

A chromium stock solution (1,000 mg·L$^{-1}$) is prepared by dissolving 2.83 g of $K_2Cr_2O_7$ in 1 L of double distilled water and diluting to the desired concentration.

### 2.2. Preparation of biosorbent

Peanut shells are washed several times with pure water to remove dust and soluble impurities attached to the surface. The washing operation is repeated until the washing water becomes uncolored. The washed peanut shells are dried in a hot air oven to remove moisture at 105°C for 12 h, and then they are ground and sieved using a standard sieve to obtain biosorbents with homogeneous and known particle sizes: 1 mm, 500 μm, 250 μm and 125 μm. Recovered samples are saved in closed bottles for later use. The resulting material is named peanut shell powder (PSP).

### 2.3. Biosorbent characterization

For the pH measurement of the PSP biosorbent, 3 g of the powder are placed in a beaker; a volume of double-distilled water has been added so that the solid is completely wetted. The mixture was stirred for 15 min, and then the pH of the supernatant solution is measured. The pH measurements were done using Hanna Instruments pH 210. Also, proximate analyses of the peanut shells samples were conducted using conventional ASTM standard methods. For this purpose, ASTM D-6683 and ASTM D-4442 were used to determine bulk density and moisture content of the PSP biomass, respectively.

Chemical properties and microscopic appearance of peanut shells biomaterial are studied by FTIR and SEM. SEM (Quanta 250 from FEI) is utilized to observe the microstructure and morphology of the PSP biosorbent. Therefore, (JASCO FTIR 4100) is used to collect spectra in the range of 400–4000 cm$^{-1}$ wave-number. First, the peanut shell samples are mixed with KBr, then compressed into tablets before recording the FTIR spectrum. The background obtained by pure KBr scanning is automatically subtracted from the sample spectrum.

### 2.4. Adsorption studies

#### 2.4.1. Batch sorption experiments

Batch experiments are carried out to reveal the adsorption capacity of PSP biomass for Cr(VI), which are conducted according to a typical jar test procedure (Fig. 1). All the experiments are performed at room temperature (25°C ± 2°C). For each of the six test jar beakers, A weight $m$ of the biosorbent is added to 250 mL of the Cr(VI) solution with an initial concentration of $C_0$. The pH experiments are realized using 0.1 M HCl/NaOH to vary the solution pH. The effect of operational parameters on the performance of chromium biosorption by SPS was studied by varying the values of these parameters as shown: particle size 1 mm, 500 μm, 250 μm

Fig. 1. Jar test procedure.

and 125 μm; contact time 20–100 min; pH 1.5–6; stirring speed 100 and 300 rpm; biosorbent dosage 0.5–3.5 g and initial concentration of Cr(VI) 20–70 mg·L$^{-1}$. The selection of the range of biosorption parameters is based on previous similar scientific work on biosorption of chromium from aqueous solutions. The residual concentration of Cr(VI) is determined by UV-Vis spectrophotometer using 1,5-diphenylcarbazide method [21]. The amount of Cr(VI) adsorbed $Q_e$ (mg·g$^{-1}$) and removal percentage ($R$%) are calculated by the following equations:

$$Q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where $C_e$ is the equilibrium Cr(VI) concentrations (mg·L$^{-1}$), $C_0$ is the initial Cr(VI) concentrations (mg·L$^{-1}$), $m$ is the weight of adsorbent (g) and $V$ is the volume of the Cr(VI) solution (L). All experiments are repeated three times and the average value is taken. The residual concentration of Cr(VI) is measured at 540 nm using the 1,5-diphenylcarbazide method with an UV-vis spectrophotometer (JENWAY 6300).

### 2.4.2. Adsorption isotherms

The Langmuir [48] and Freundlich [49] isotherm equilibrium models are used to describe the adsorption mechanism of Cr(VI) on the surface of the PSP biosorbent.

Langmuir's model reveals that the adsorption takes place on a homogeneous surface by monolayer sorption without interactions between the adsorbed molecules. The following equation represents the linear form of the Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bC_e q_{\max}} \tag{3}$$

where $q_{\max}$, $q_e$, $C_e$ and $b$ are the maximum sorption capacity (mg·g$^{-1}$), the mass of sorbed at equilibrium (mg·g$^{-1}$), the equilibrium concentration of adsorbate (mg·L$^{-1}$) and sorption equilibrium constant (L·mg$^{-1}$), respectively. For Langmuir sorption, the separation factor ($R_L$) is used to define the type of isotherm and is expressed in Eq. (4) [22].

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

Therefore, the value of ($R_L$) indicates whether the adsorption process is favorable or unfavorable. This process is irreversible for $R_L = 0$, linear for $R_L = 1$, favorable for $R_L < 1$, and unfavorable for $R_L > 1$ [23].

The Freundlich isotherm model shows that there is also a monolayer sorption, but the energy distribution of the active sites is not homogeneous with the presence of interactions between the adsorbed molecules. The logarithmic form of the model is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where $q_e$, $C_e$, $K_F$ and $1/n$ are the maximum amount of metal ions per unit weight of the biosorbent, the equilibrium Cr(VI) ion concentration in the solution, the sorption capacity per unit concentration and the sorption intensity, respectively. The value of $1/n$ indicates that the type of isotherm is favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$) and irreversible ($1/n = 0$) [24].

### 2.4.3. Kinetics of biosorption

The pseudo-first-order [Eq. (6)] and second-order [Eq. (7)] kinetic models presented below are applied to characterize the kinetics of the sorption reaction of Cr(VI) by the PSP biosorbent [25,26].

$$\log(q_e - q_t) = \frac{K_1}{2.303}t + \log q_e \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2} \tag{7}$$

where $q_t$ and $q_e$ represent the sorption capacities (mg·g$^{-1}$) of PSP biosorbent at any time $t$ (min) and at equilibrium, respectively. The first and second-order kinetic rate constants are noted by $K_1$ (min$^{-1}$) and $K_2$ (mg$^{-1}$·g$^{-1}$·min$^{-1}$). The pseudo-first-order kinetic model is established by tracing the log($q_e - q_t$) value vs. time ($t$) to determine the values of $q_e$, $K_1$ and $R^2$. However, the pseudo-second-order kinetic model is established by plotting the value of $t/q_t$ against time ($t$) to determine the values of $q_e$, $K_2$ and $R^2$. The regression coefficients ($R^2$) of the first-order and second-order kinetic models are compared to determine which model is more adequate for the sorption of Cr(VI) by the PSP biosorbent.

## 3. Results and discussion

### 3.1. Biosorbent characterization

The results of some physical analysis are presented in Table 1. According to the ASTM standard, the average bulk density and moisture content of the peanut shells used in this study are 0.25 g·cm$^{-3}$ and 6%, respectively, while their pH is 7.5.

### 3.2. FTIR spectroscopy

Previous studies have shown that the adsorption mechanism of hexavalent chromium by agricultural wastes can be caused by surface precipitation, physical adsorption, ion exchange, complexation with functional groups and chemical reactions with surface sites [27]. Several researchers have indicated that different chemical functional groups such as hydroxyl, carboxyl, amide, etc., are responsible for the biosorption of metal ions [28–31]. The functional groups are the sites susceptible to the biosorption process, and the metal retention capacity depends on various factors such as the accessibility of these sites, their abundance, their chemical state and the attraction between the adsorption site and the metal. FTIR spectroscopy is a very important analytical technique for detecting the vibrational characteristics of the chemical functions present on the biosorbent surfaces. The FTIR method is used to verify the surface chemistry of PSP biosorbent, and the results are shown in Fig. 2. On the other hand, Table 2 presents the principal vibration frequencies and their corresponding groups. Obviously, the surface of the PSP biosorbent contains different chemical functions, such as (O–H, C–O, C=O and C–H). Thus, the existence of interactions between Cr(VI) ions and the different functional groups present on the surface of biosorbents such as –OH, C–C, C–H, C–O, C–O–C and C=O, has been demonstrated in previous work [32]. Consequently, the FTIR analysis shows that the peanut shells used in this study has surface functional groups capable of playing an important role in the removal of chromium(VI) ions.

Table 1
Some physical properties of peanut shell used in this study

| | |
|---|---|
| Moisture, % | 6 |
| Bulk density, g·cm$^{-3}$ | 0.25 |
| pH | 7.5 |

### 3.3. SEM characterization

The morphology and microstructure of the PSP biosorbent are presented in Fig. 3. It can be seen from the SEM photos that the external morphology of PSP has a rather rough, irregular, coarse and porous surface. The nature of the biosorbent is due to abundant amount of functional groups present on its surface [32]. On this basis, the PSP image can be clearly shown that the surface is adapted to Cr(VI) adsorption.

### 3.4. Conventional experimental variables of biosorption

In this section, the influence of different experimental variables such as solution pH, biosorbent dose, initial metal

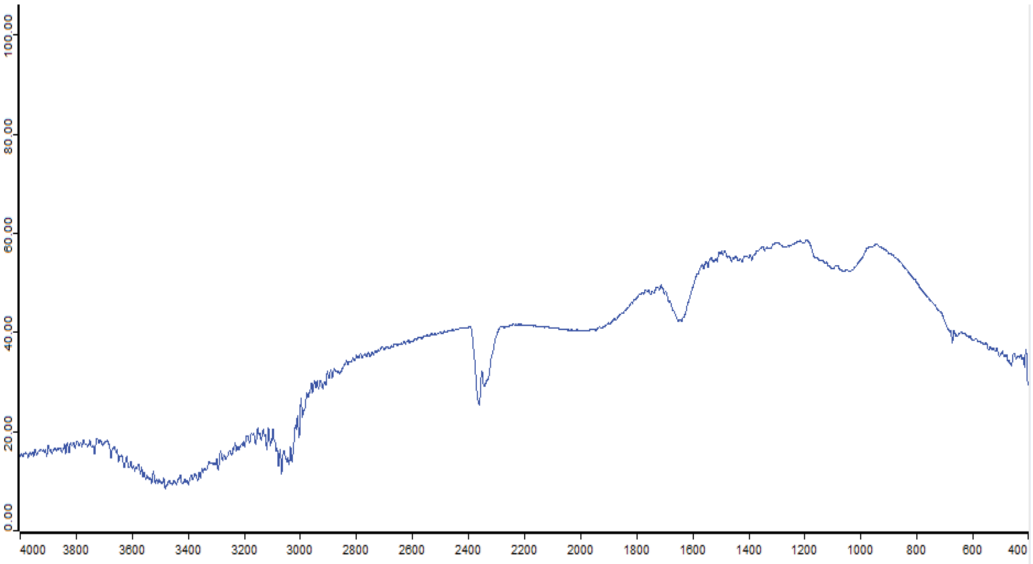

Fig. 2. FTIR spectra of peanut shells biomass.

Table 2
Infrared principal absorption bands of peanut shell biomass and their corresponding groups

| Wavenumbers (cm$^{-1}$) | Functional groups |
|---|---|
| 3,069 | C–H stretching in aliphatic |
| 2,050 | C=O (carbonyl) bond of the aldehydes, ketonic and acetyl groups |
| 1,638 | C=O stretching in carboxyl or amide groups |
| 1,083 | C–O: stretching vibrations of functional groups such as esters, carboxylic acids, ethers and alcohols |
| 663 | O–H vibrations group |

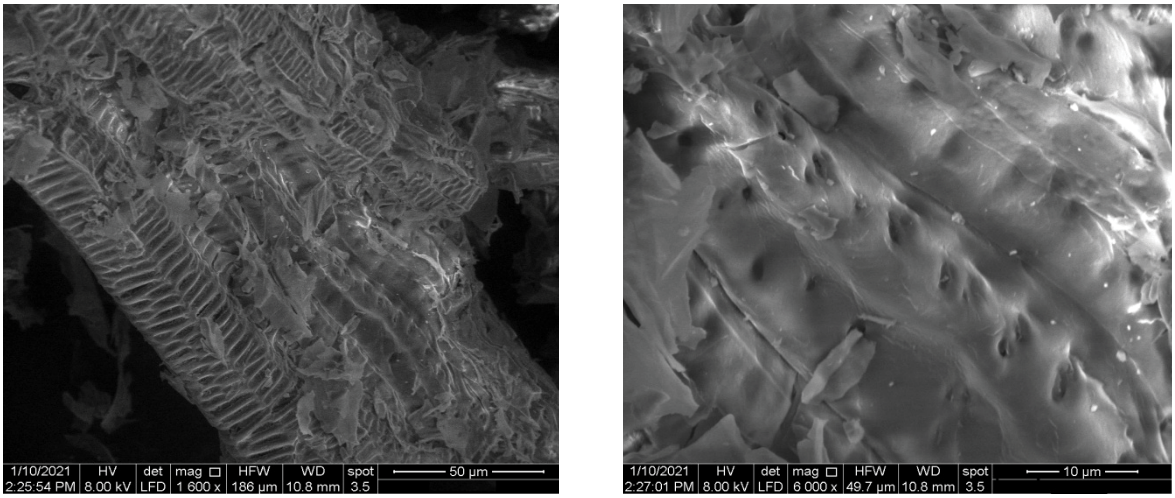

Fig. 3. SEM images of PSP biomass.

ion concentration, particle size and stirring speed which are used to optimize the appropriate experimental conditions for maximum metal removal by the peanut shell biosorbent. For each biosorption experiment, aqueous samples were collected at different time intervals of 20, 40, 60, 80, and 100 min to estimate the biosorption capacity of PSP during these treatments periods.

### 3.5. Impact of particle size

The adsorption of Cr(VI) on the PSP biosorbent is studied at four different particle sizes: 1 mm, 500 µm, 250 µm and 125 µm. As shown in Fig. 4, the adsorption capacity increases as the particle size of the adsorbent decreases. Cr(VI) ions may not be able to penetrate some of the internal pores of the particles since access to all pores is facilitated by the small size of the particles [33]. Particles < 125 µm shows the greatest adsorption capacity.

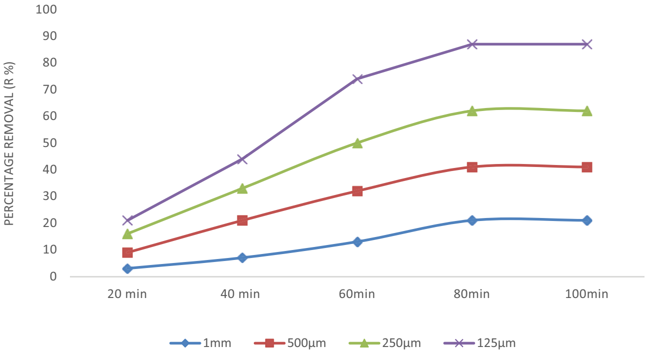

Fig. 4. Effect of particle size on Cr(VI) biosorption (Cr(VI) initial concentration: 10 $mg·L^{-1}$, pH: 5.4, contact time: 100 min, stirring speed: 300 rpm, and biosorbent dosage: 2 g).

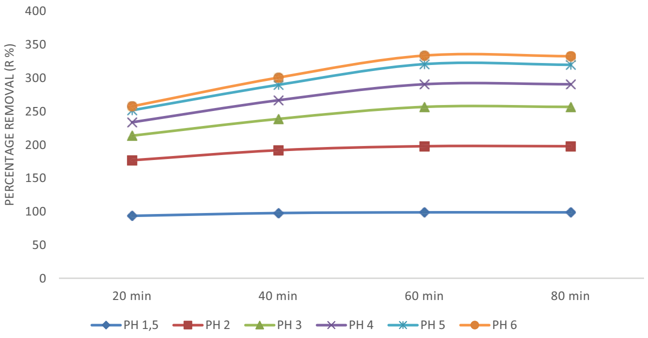

Fig. 5. Effect of pH on Cr(VI) biosorption (initial Cr(VI) concentration: 10 $mg·L^{-1}$, particle size 125 µm, contact time: 80 min, stirring speed: 300 rpm, and biosorbent dosage: 2 g.

### 3.6. Impact of pH on Cr(VI) biosorption

The biosorption of heavy metals in aqueous solutions depends on the characteristics of the biosorbent and the transfer of adsorbate molecules from the solution to the solid phase. Previous studies have shown that the most important parameter to affect the biosorption process is pH [34]. The analysis of the pH dependence for the sorption of Cr(VI) ions by PSP is performed in order to identify the optimal pH for the biosorption operations. Generally, the working pH value affects the charge properties of the adsorbed molecules and the surface of the adsorbent [35]. The effect of $H^+$ ions concentration on the biosorption of Cr(VI) ions is studied on PSP in the pH range of 1.5–6. It was found that maximum biosorption of Cr(VI) occurs at an initial pH ranging from 1.5 to 2 with values of 99% and 98%, respectively and decreases at higher pH values as shown in Fig. 5. In addition, the biosorption capacity of PSP was reduced from 98% to 29% with an increase in pH from 2 to 6. Chromium exists mainly as $HCrO_4^-$ in this very acidic medium with a low net negative charge. This promotes the easy binding of chromium ions to the surface of the PSP absorbent. On the other hand, a strong decrease in biosorption above pH 4 may be due to the occupation of the adsorption sites by oxy-anionic species such as $HCrO_4^-$, $Cr_2\,O_7^{2-}$, $CrO_4^{2-}$, etc., which prevents the approach of the Cr(VI) ions to the sorbent surface. In conclusion, the limited adsorption of Cr(VI) at pH values higher than 4 is due to competition between OH and the oxyanion of Cr(VI); this leads to repulsive forces between Cr(VI) anions and the biosorbent surface [34].

The pH dependence of metal sorption may be related to the presence of several functional groups (such as carboxyl, amino, amide and phosphate, etc.) on the biosorbent surface [30]. It has also been noted that biosorption capacities of heavy metals are highly sensitive to pH and that the extent of biosorption reduced as the pH of the solution increases [28,32,36–38].

In general, industrial wastewater containing Cr(VI) ions has a high acidic pH, so no pH adjustment would be necessary before treating this wastewater with PSP biosorbent. Therefore, the maximum value of the adsorption capacity of the PSP biosorbent occurs at pH of 1.5. As a result, the pH value of 1.5 is used as the optimal pH value for further biosorption experiments to determine the optimal value of other parameters.

### *3.7. Impact of biosorbent dose*

The dose of biosorbent is a very important parameter because it promotes the uptake of heavy metals in aqueous solution. The Results of dosage effect on the removal of Cr(VI) ions by SPS are shown in Fig. 6. The influence of the biosorbent dose on the sorption of Cr(VI) ions was investigated in the range of 0.5–3.5 g·L$^{-1}$. These results indicate that the percentage of Cr(VI) biosorption increases with the rise of the amount of biosorbent, but above a certain value, the percentage of removal reaches a saturation level. This percentage increases from 77% to 98% when the dose is increased from 0.5 to 1.5 g·L$^{-1}$. The mechanism can be justified by the fact that the incremental PSP dosage values increased the availability of more active sites for Cr(VI) ion uptake, leading to a better efficiency in the removal of metal ions [39,40]. However, as the amount of biosorbent increased further, the sorption of Cr(VI) did not increase but remained constant, which is shown in Fig. 6. The various interpretations given include a less available binding site, competition between chromium ions, agglomeration of the adsorption site, electrostatic interaction, inadequate mixing due to higher biomass density [41].

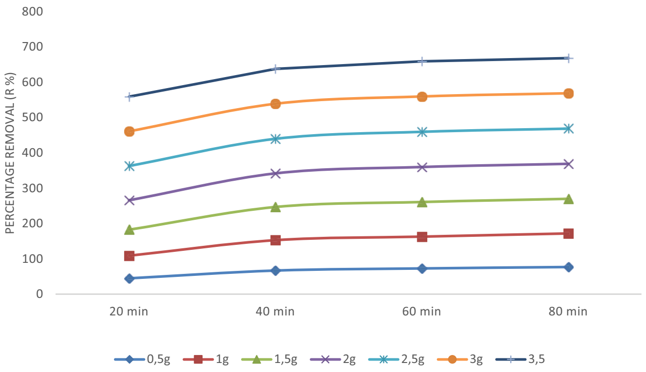

Fig. 6. Effect of biosorbent dose on Cr(VI) biosorption (initial Cr(VI) concentration: 10 mg·L$^{-1}$, particle size 125 μm, contact time: 80 min, stirring speed: 300 rpm, and pH: 1.5).

### *3.8. Impact of agitation speed*

The stirring speed also has a significant impact on the mass transfer process of Cr(VI) from the aqueous solution to the surface of the biosorbent. Fig. 7 describes the capacity of PSP biosorbent to remove Cr(VI) from three different concentrations (20, 40 and 60 mg·L$^{-1}$) at various rpm (100 and 300). The biosorption capacity of PSP for Cr(VI) increases with the increase of stirring speed. When the stirring speed is changed from 100 to 300, the percentage removal of Cr(VI) increases from (98%, 90% and 80.6%) to (99.8%, 94% and 85%), respectively. This can be explained by an increase in the rate of diffusion of Cr(VI) ions on the surface of the biosorbent with increasing agitation speed [33].

### *3.9. Impact of concentration of Cr(VI) on biosorption*

For a better management of the cost-effectiveness of industrial wastewater treatment for Cr(VI) removal, the required solute/sorbent ratio must be known. Under the conditions of optimal pH, biosorbent dosage and stirring speed of 1.5, 2.5 g and 300 rpm, respectively, the capture performance of PSP biosorbent for chromium ions is investigated experimentally. The concentration of Cr(VI) solution ranges from 10 to 70 mg. Fig. 8 shows the removal percentage at different Cr(VI) concentrations. As shown in Fig. 8, the rate

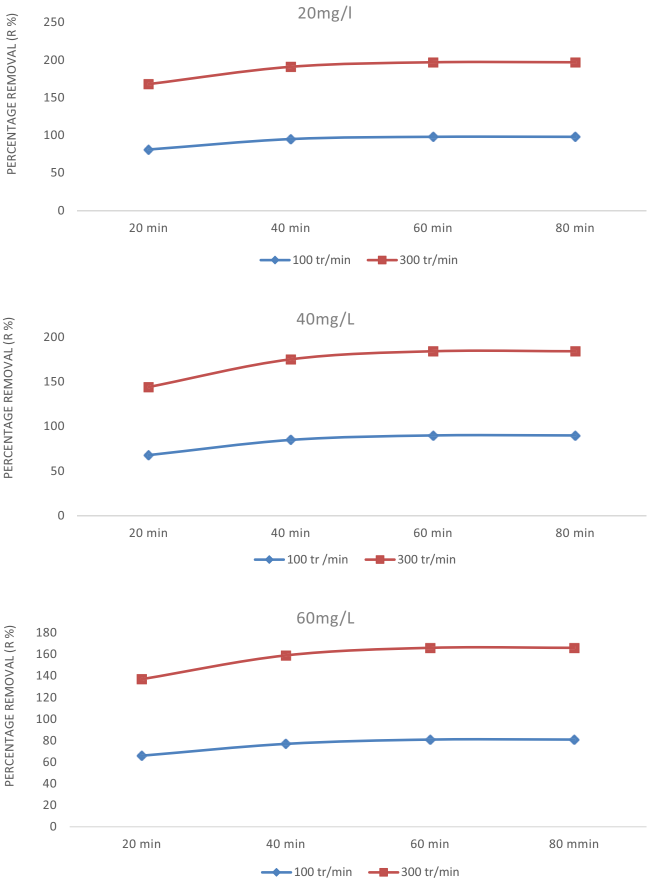

Fig. 7. Effect of agitation speed on Cr(VI) biosorption (initial Cr(VI) concentration: 20, 40, 60 mg·L$^{-1}$, particle size 125 μm, contact time: 80 min, pH: 1.5, and biosorbent dosage: 2.5 g).

of Cr(VI) biosorption decreases with increasing Cr(VI) concentration, at a low concentration (10 mg·L$^{-1}$), the percentage removal by PSP biosorbent is 99.98%. This can be explained by the improving in the concentration gradient between the aqueous and the solid phase [42] and also because of a competition between sorbate ions for their fixation on the active sites available on the surface of the biomaterial [36].

On the other hand, we can observe a preliminary fast rate of biosorption capacity of Cr(VI) ions followed by a secondary slow rate. In the initial biosorption periods, the availability of a huge amount of active sites allowed a better fixation of Cr(VI) ions on the surface of the PSP biosorbent. This resulted in a strong increase in biosorption capacity during the first 40 min of contact time for all initial Cr(VI) ion concentrations. After this period of time, the surface of the PSP is completely saturated and no more chromium uptake is possible, which meant reaching equilibrium for biosorption [43].

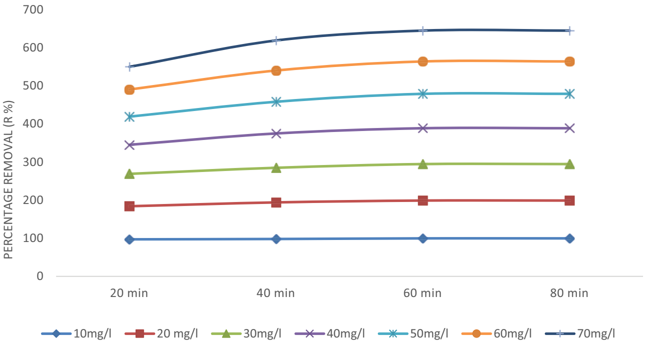

Fig. 8. Effect of initial concentration on Cr(VI) biosorption (particle size 125 μm, contact time: 80 min, stirring speed: 300 rpm, pH: 1.5, and biosorbent dosage: 2.5 g).

### 3.10. Sorption kinetic modeling

The biosorption kinetics studies were performed by changing the initial concentration (30 and 60 mg·L$^{-1}$) while keeping the other parameters constant (agitation speed: 300 rpm, biosorbent dosage: 2.5 g, temperature: 25°C ± 2°C, pH: 1.5, adsorbent size: 125 μm) at an interval of 20 min for a period of 80 min. Figs. 9 and 10 show the pseudo-first-order and pseudo-second-order kinetic plots, respectively.

Adsorption kinetics provides important information on the temporal interactions between the solid and fluid phases of the adsorption system, which is essential for the design and industrial extension of the process [44]. For the present work, pseudo-first-order and pseudo-second-order models are examined in order to understand the kinetics of Cr(VI) biosorption by PSP. Table 3 shows the constant rate ($K_1$, $K_2$), $q_e$ values and regression coefficient $R^2$ for the PSP biosorbent. A comparison between the two kinetics models shows

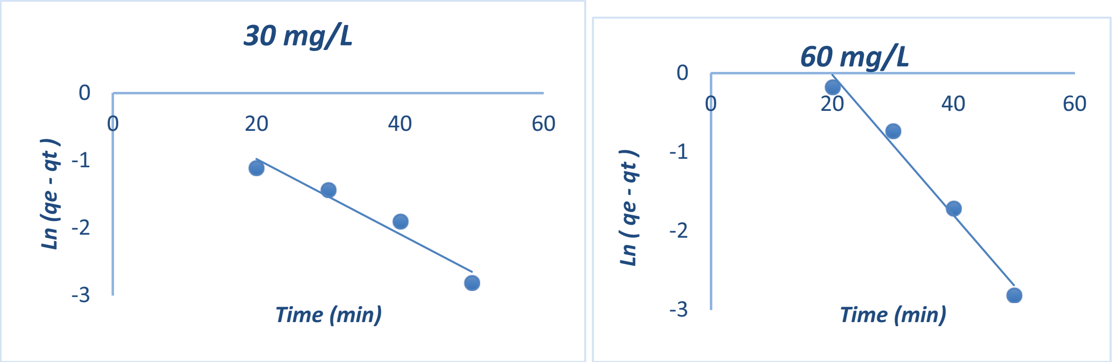

Fig. 9. Plot of pseudo-first-order kinetic model.

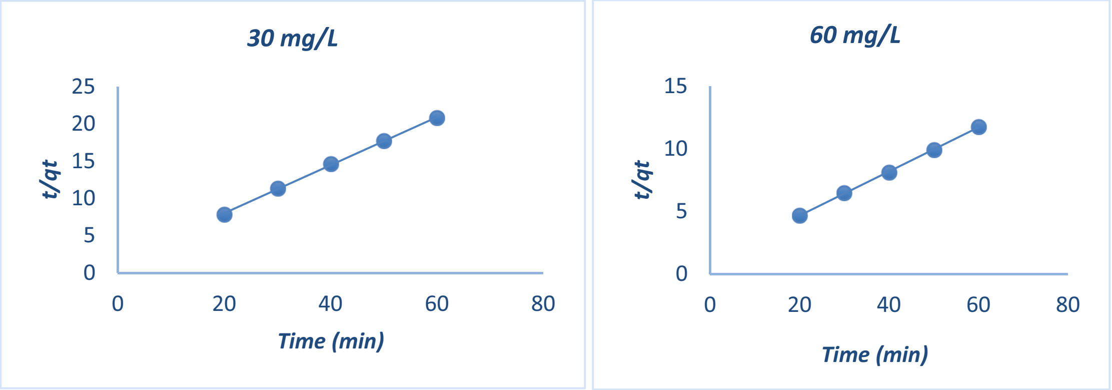

Fig. 10. Plot of pseudo-second-order model.

that the Cr(VI) sorption by peanut shells follows closely the kinetics of pseudo-second-order more than that of pseudo-first-order, because the value of the pseudo-second-order model coefficient ($R^2$) is very slightly higher than that of pseudo-first-order.

The pseudo-first-order kinetic model supposes that "the sorption process of metals is first order in nature because it only depends on the number of metal ions in solution at a specific time" [26]. Contrary to the pseudo-first-order kinetic model, the pseudo-second-order kinetic model considers that "the process of metal biosorption depends on the number of metal ions in solution as well as on the biosorption sites available on the surface of the biosorbent" and shows that the occupancy rate of adsorption sites is proportional to the square of unoccupied sites [45]. Thus, it has been concluded that the chemisorption mode can control the biosorption process with the implication of electron exchanges [43].

### *3.11. Sorption isotherm modeling*

In this study, the Freundlich and Langmuir adsorption isotherms are used to model the adsorption in aqueous media of Cr(VI) ions by the PSP biosorbent, using the experimental results obtained to study the impact of the initial concentration on the adsorption capacity of PSP. Both of these classical adsorption models are used to describe the equilibrium between chromium ions adsorbed on the biomaterial surface ($q_e$) and chromium metal ions in solution ($C_e$). The constants of the two models are determined from the slopes and intercepts of the linear graphs, as shown in Fig. 11.

The Langmuir isotherm represents a system in which adsorption is performed on a monolayer surface without interaction between the adsorbent and the adsorbed ions [46]. The Freundlich isotherm characterizes a system in which non-ideal adsorption occurs on a heterogeneous surface with the presence of polyfunctional groups and different interactions [47]. The values of the different parameters related to each of the two equilibrium models are given in Table 4. According to the correlation values of the two isotherms studied, it was found that the data on the sorption of Cr(VI) ions by PSP biomaterial can be well adjusted to the Freundlich and Langmuir isotherm models with a regression value of >0.96. The linear conversion of the adsorption results using the Langmuir and Freundlich models ($R^2 > 0.96$) allowed the calculation of the Cr(VI) adsorption capacities. It was found that the experimental data obtained in this study obeyed the basic principles of these two models that is, monolayer adsorption with constant adsorption energy and heterogeneous surface adsorption, respectively [48,49].

Table 3
Kinetics parameters for Cr(VI) sorption by PSP biosorbent

| Initial Cr(VI) concentration (mg·L$^{-1}$) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|---|
| | $q_e$ (mg·g$^{-1}$) | $K_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg·g$^{-1}$) | $K_2$ (g·mg$^{-1}$·min$^{-1}$) | $R^2$ |
| 30 | 1.1468 | 0.0557 | 0.9445 | 3.0769 | 0.0694 | 0.991 |
| 60 | 5.7822 | 0.0888 | 0.9805 | 5.6915 | 0.0264 | 0.997 |

Table 4
Values of equilibrium parameters for the adsorption of Cr(VI) on the PSP biosorbent

| Freundlich isotherm | | | Langmuir isotherm | | | |
|---|---|---|---|---|---|---|
| $R^2$ | $1/n$ | $K_F$ (L·mg$^{-1}$) | $R^2$ | $q_m$ (mg·g$^{-1}$) | $b$ | $R_L$ ($C_0$ = 50 mg·L$^{-1}$) |
| 0.9977 | 0.2622 | 2.81 | 0.9695 | 4.11 | 16 | 0.0013 |

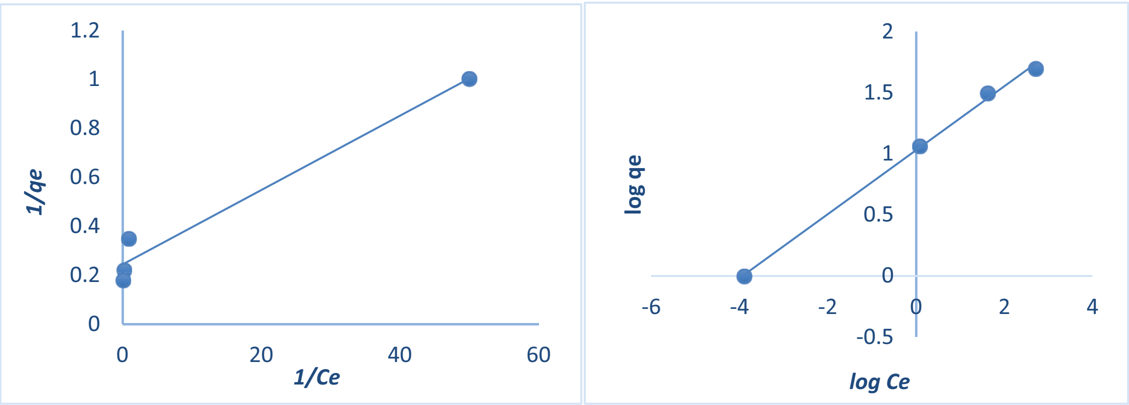

Fig. 11. Langmuir and Freundlich sorption isotherms of chromium Cr(VI) ions on PSP biosorbent.

Based on the value of $R_L$ for this study ($R_L = 0.0013 < 1$) which means that the sorption process of Cr(VI) is favorable. Knowing that the sorption process is unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and irreversible ($R_L = 0$) [48,50].

## 4. Conclusion

Peanut shell biomass is a potential ecological biosorbent for heavy metals. This work investigated the effectiveness of this biomaterial in removing Cr(VI) ions from an aqueous solution. It has been found that the biosorption process depends on the pH of the solution, pH 1.5 being the optimal value. Increasing the amount of biosorbent increases the percentage removal of metal ions. The current results show that the data on sorption of Cr(VI) ions by PSP biomass can be well adapted to the Freundlich and Langmuir isotherm models with a regression value of >0.96 within the investigated concentration range. The kinetic study of equilibrium data shows that the biosorption of Cr(VI) on PSP follows well the pseudo-second-order kinetic model. Therefore, it can be concluded that peanut shell biosorbent has great potential and can be used to effectively and economically remove hexavalent chromium from aqueous solutions. In addition, the PSP biosorbent appears to be effective at low concentrations of metals under optimal conditions. However, further studies are necessary to extend the research to field applications. Therefore, similar adsorption experiments can be conducted to obtain the adsorption capacity of PSP biomass for the removal of other pollutants.

## References

[1] E. Aseman-Bashiz, A. Rezaee, G. Moussavi, Effective removal of hexavalent chromium using microbial cellulose/polyaniline cathode and nanosized $FeS_2$ in the form of an integrated electrochemical system, J. Water Process Eng., 44 (2021) 102333, doi: 10.1016/j.jwpe.2021.102333.

[2] M.E. Mahmoud, S.M. Elsayed, S.E.M.E. Mahmoud, R.O. Aljedaani, M.A. Salam, Recent advances in adsorptive removal and catalytic reduction of hexavalent chromium by metal–organic frameworks composites, J. Mol. Liq., 347 (2022) 118274, doi: 10.1016/j.molliq.2021.118274.

[3] M. Balali-Mood, K. Naseri, Z. Tahergorabi, M.R. Khazdair, M. Sadeghi, Toxic mechanisms of five heavy metals: mercury, lead, chromium, cadmium, and arsenic, Front. Pharmacol., 12 (2021) 227, doi: 10.3389/fphar.2021.643972.

[4] N. Lu, T. Hu, Y. Zhai, H. Qin, J. Aliyeva, H. Zhang, Fungal cell with artificial metal container for heavy metals biosorption: equilibrium, kinetics study and mechanisms analysis, Environ. Res., 182 (2020) 109061, doi: 10.1016/j.envres.2019.109061.

[5] T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J., 118 (2006) 83–98.

[6] D. Mohan, S. Rajput, V.K. Singh, P.H. Steele, C.U. Pittman Jr., Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent, J. Hazard. Mater., 188 (2011) 319–333.

[7] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater., 87 (2001) 273–287.

[8] M.J. Rivero, O. Primo, M.I. Ortiz, Modelling of Cr(VI) removal from polluted groundwaters by ion exchange, J. Chem. Technol. Biotechnol., 79 (2004) 822–829.

[9] M.A. Barakata, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, Desalination, 256 (2010) 90–93.

[10] C.A. Kozlowski, W. Walkowiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, Water Res., 36 (2002) 4870–4876.

[11] N. Bouchemal, Y. Azoudj, Z. Merzougui, F. Addoun, Adsorption modeling of Orange G dye on mesoporous activated carbon prepared from Algerian date pits using experimental designs, Desal. Water Treat., 45 (2012) 284–290.

[12] N. Bouchemal, F. Addoun, Adsorption of dyes from aqueous solution onto activated carbons prepared from date pits: the effect of adsorbents pore size distribution, Desal. Water Treat., 7 (2009) 242–250.

[13] A.A. Attia, B.S. Girgis, N.A. Fathy, Removal of methylene blue by carbons derived from peach stones by $H_3PO_4$ activation: batch and column studies, Dyes Pigm., 76 (2008) 282–289.

[14] M.J. Martin, A. Artola, M.D. Balaguer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, Chem. Eng. J., 94 (2003) 231–239.

[15] C. Kirbiyik, A.E. Putun, E. Putun, Comparative studies on adsorptive removal of heavy metal ions by biosorbent, biochar and activated carbon obtained from low cost agro-residue, Water Sci. Technol., 73 (2016) 423–436.

[16] Z. Yousefi, A. Mashayekh-Salehi, R.A. Mohammadpour Tahmtan, Biosorption of chromium in aqueous solutions using bivalve mollusk shells through central composite design (CCD) model, Desal. Water Treat., 42 (2015) 19877–19889.

[17] P. Das Saha, A. Dey, P. Marik, Batch removal of chromium(VI) from aqueous solutions using wheat shell as adsorbent: process optimization using response surface methodology, Desal. Water Treat., 39 (2012) 95–102.

[18] K. Nithya, A. Sathish, P. Senthil Kumar, T. Ramachandran, Biosorption of hexavalent chromium from aqueous solution using raw and acid-treated biosorbent prepared from *Lantana camara* fruit, Desal. Water Treat., 52 (2016) 25097–25113.

[19] A. Saravanan, P. Senthil Kumar, B. Preetha, Optimization of process parameters for the removal of chromium(VI) and nickel(II) from aqueous solutions by mixed biosorbents (custard apple seeds and *Aspergillus niger*) using response surface methodology, Desal. Water Treat., 57 (2016) 14530–14543.

[20] E. Suganya, S. Rangabhashiyam, A.V. Lity, N. Selvaraju, Removal of hexavalent chromium from aqueous solution by a novel biosorbent *Caryota urens* seeds: equilibrium and kinetic studies, Desal. Water Treat., 57 (2016) 23940–23950.

[21] S.M. Prabhu, M. Subaramanian, S. Meenakshi, A simple one-pot in-situ method for the synthesis of aluminum and lanthanum binary oxyhydroxides in chitosan template towards defluoridation of water, Chem. Eng. J., 283 (2016) 1081–1089.

[22] M. Arulkumar, K. Thirumalai, P. Sathishkumar, T. Palvannan, Rapid removal of chromium from aqueous solution using novel prawn shell activated carbon, Chem. Eng. J., 185–186 (2012) 178–186.

[23] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, J. Hazard. Mater., 123 (2005) 223–231.

[24] E.R. Alley, Water Quality Control Handbook, McGraw-Hill Companies, Inc, WEF PRESS Water Environment Federation Alexandria, Virginia, 2007.

[25] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsa-Kademiens. Handlingar, 24 (1898) 1–39.

[26] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[27] M. Jain, V.K. Garg, K. Kadirvelu, Chromium(VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste, J. Hazard. Mater., 162 (2009) 365–372.

[28] X. Han, Y.S. Wong, M.H. Wong, N.F.Y. Tama, Biosorption and bioreduction of Cr(VI) by a microalgal isolate *Chlorella miniata*, J. Hazard. Mater., 146 (2007) 65–72.

[29] M.Y. Arica, G. Bayramoglu, Cr(VI) biosorption from aqueous solutions using free and immobilized biomass of *Lentinus sajor-caju*: preparation and kinetic characterization, Colloids Surf., A, 253 (2005) 203–211.

[30] S. Tunali, K. Ismail, T. Akar, Chromium(VI) biosorption characteristics of *Neurospora crassa* fungal biomass, Miner. Eng., 18 (2005) 681–689.

[31] R. Nadeem, T.M. Ansari, A.M. Khalid, Fourier transform infrared spectroscopic characterization and optimization of Pb(II) biosorption by fish (*Labeo rohita*) scales, J. Hazard. Mater., 156 (2008) 64–73.

[32] K. Rambabu, G. Bharath, F. Banat, P.L. Show, Biosorption performance of date palm empty fruit bunch wastes for toxic hexavalent chromium removal, Environ. Res., 187 (2020) 109694, doi: 10.1016/j.envres.2020.109694.

[33] G. McKay, M.S. Otterburn, A.G. Sweeny, The removal of colour from effluent using various adsorbents—IV. Silica: equilibria and column studies, Water Res., 14 (1980) 21–27.

[34] V. Vinodhini, N. Das, Mechanism of Cr(VI) biosorption by neem sawdust, Am. Eurasian J. Sci. Res., 4 (2009) 324–329.

[35] M. Daoud, O. Benturki, P. Girods, A. Donnot, S. Fontana, Adsorption ability of activated carbons from *Phoenix dactylifera rachis* and *Ziziphus jujube* stones for the removal of commercial dye and the treatment of dyestuff wastewater, Microchem. J., 148 (2019) 493–502.

[36] K. Rambabu, A. Thanigaivelan, G. Bharath, N. Sivarajasekar, F. Banat, P.L. Show, Biosorption potential of *Phoenix dactylifera* coir wastes for toxic hexavalent chromium sequestration, Chemosphere, 268 (2021) 128809, doi: 10.1016/j.chemosphere.2020.128809.

[37] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*, Chem. Eng. J., 117 (2006) 71–77.

[38] X.S. Wang, Y.P. Tang, R.T. Sheng, Kinetics, equilibrium and thermo dynamics study on removal of Cr(VI)from aqueous solutions using low-cost adsorbent Alligator weed, Chem. Eng. J., 148 (2008) 217–225.

[39] N. Sivarajasekar, R. Baskar, Adsorption of Basic red 9 on activated waste *Gossypium hirsutum* seeds: process modeling, analysis and optimization using statistical design, J. Ind. Eng. Chem., 20 (2014) 2699–2709.

[40] S.R. Bai, T.E. Abraham, Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*, Bioresour. Technol., 79 (2001) 73–81.

[41] E. Malkoc, Y. Nuhoglu, Investigations of nickel(II) removal from aqueous solutions using tea factory waste, J. Hazard. Mater., 127 (2005) 120–128.

[42] N. Sivarajasekar, R. Baskar, Adsorption of Basic Magenta II onto $H_2SO_4$ activated immature *Gossypium hirsutum* seeds: kinetics, isotherms, mass transfer, thermodynamics and process design, Arabian J. Chem., 12 (2019) 1322–1337.

[43] A. ul Haq, M. Saeed, M. Usman, S.A.R. Naqvi, T.H. Bokhari, T. Maqbool, H. Ghaus, T. Tahir, H. Khalid, Sorption of chlorpyrifos onto zinc oxide nanoparticles impregnated Pea peels (*Pisum sativum* L): equilibrium, kinetic and thermodynamic studies, Environ. Technol. Innov., 17 (2020) 100516, doi: 10.1016/j.eti.2019.100516.

[44] K. Rambabu, F. Banat, G.S. Nirmala, S. Velu, P. Monash, G. Arthanareeswaran, Activated carbon from date seeds for chromium removal in aqueous solution, Desal. Water Treat., 156 (2019) 267–277.

[45] Y.S. Ho, G. Mckay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 34 (2000) 736–742.

[46] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J., 156 (2010) 2–10.

[47] Z. Lu, Y. Liu, S. Liu, Y. Yin, G. Zeng, X. Tan, X. Hu, X. Hu, L. Jiang, Y. Ding, S. Liu, X. Huang, Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures, Bioresour. Technol., 218 (2016) 351–359.

[48] J. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[49] H. Freundlich, Colloid and Capillary Chemistry, Methuen, London, 1926.

[50] H. Freundlich, Über die Adsorption in Lösungen, Z. Phys. Chem., 57 (1907) 385–470.