



Research Article



Comparative study of the effective removal of hexavalent chromium via calcium alginate and calcium alginate/*Ulva fasciata* composite

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Abstract

The present study revealed for the first time the removal of hexavalent chromium Cr(VI) with a high efficiency using an eco-friendly composite beads of alginate with the green alga *Ulva fasciata* compared to calcium alginate beads. This conclusion was reached in this study from the comparison of the removal efficiency of Cr(VI) by the well-known biosorbent material, calcium alginate (CA) with the studied calcium alginate/*Ulva fasciata* (CA/UF) biocomposite beads. The characterization of the prepared beads was achieved using several techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray (EDAX). The Brunauer, Emmett, Teller (BET) and Barrett, Joyner, Halenda (BJH) analyses were also employed which indicated a three-fold increase in the surface area, a mean pore diameter of 2.3-fold and a total pore volume of 14-fold for calcium alginate/*Ulva fasciata* composite compared to calcium alginate beads. The results of batch experiments demonstrated the fast complete removal of Cr(VI) by the CA/UF composite compared to the maximum removal (75%) by CA. The Dubinin–Radushkevich isotherm model reflected the physical pore volume filling of Cr(VI) rather than adsorption on the pore walls, giving an adsorption mean free energy (2.24 kJ/mol) for CA/UF greater than that of CA (0.13 kJ/mol). Furthermore, Brunauer–Emmett–Teller isotherm reflected the multilayer adsorption for CA and CA/UF. Flory–Huggins isotherm model showed the more spontaneous adsorption for CA/UF than CA, with negative Gibbs free energy ΔG^0 values of -4.76 and -6.91 kJ/mol, respectively. Whereas, Temkin isotherm model showed a higher adsorption binding energy of Cr(VI) on CA/UF than CA beads. In this study, the Langmuir model of Cr(VI) adsorption on CA/UF beads was the least applied among all studied adsorption isotherm models, which also revealed the multilayer adsorption mechanism of Cr(VI) ions. The Intra-particle diffusion model was applied for CA/UF composite beads, and this application suggested that the intra-particle diffusion is a part of the rate-limiting steps. The regeneration study showed a decrease in the adsorption efficiency of CA/UF composite from 97.4 to 82.3% for three consecutive cycles.

Article Highlights

- Evaluation of the biosorption potential of calcium alginate and calcium alginate/*Ulva fasciata* composite beads.
- The surface morphology and elemental analysis of calcium alginate and calcium alginate/*Ulva fasciata* composite.
- Promising efficiency of calcium alginate/*Ulva fasciata* composite for removal of hexavalent chromium from aqueous solutions.

Keywords Alginate beads · Alginate/algae beads · Toxic heavy metal removal · Adsorption isotherms · Kinetic models · Adsorbent regeneration

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1 Introduction

Rapid industrialization has led to unregulated disposal of industrial wastes into the environment. Globally, 80% of wastewater is dumped into water bodies and industry is responsible for discharging millions of tons of heavy metals [1]. The effluents from most industries are directly discharged into the aquatic environment without any kind of treatment which leads to pollution and destruction of the ecosystem [1]. Among other pollutants, heavy metals are known for their toxicity, non-biodegradability, stability and tendency to accumulate in seawater, river, groundwater, lake, soil and sediment. Aquatic heavy metal pollution usually displays high levels of chromium (Cr), mercury (Hg), cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni) etc. in the water system [1].

Chromium exists in two stable forms namely, hexavalent chromium Cr(VI) and trivalent chromium Cr(III). Hexavalent chromium usually appears in waste from cement, stainless steel, electroplating, dyeing, and leather tanning industries as well as in wood preservation processes [2]. The United States Environmental Protection Agency (USEPA) has identified Cr(VI) as one of the seventeen chemicals that pose a threat to humans including liver dysfunction, cancer, kidney necrosis, mutagenic risks, and even death [1, 2].

The maximum acceptable concentration of chromium in drinking water is 0.05 mg/L according to the World Health Organization [3], and Agency for Toxic Substances and Disease Registry [4]. The US Environmental Protection Agency has also regulated the maximum acceptable discharge into the aquatic environment to be 0.1 mg/L [5].

Various physical and chemical methods such as electrodialysis, photocatalysis, coagulation, ion exchange, membrane separation, and chemical precipitation have been used to remove chromium from water and wastewater [2, 6–8]. Nevertheless, some of these methods have high operating costs, high energy consumption, secondary pollutant production and the difficulties in removing residual heavy metal sludge [8]. Therefore, researchers looked for alternative, sustainable, clean, eco-friendly, and green methods to sequester Cr(VI) from industrial effluents [9–11].

Biosorption is an eco-friendly technology, in which a biomaterial or a biopolymer is used as adsorbent material. It is one of the widely used methods for removing heavy metals from aqueous solutions, due to its simplicity, high efficiency and more economical technology without forming any harmful by-products [9–12]. Biosorbent materials commonly used to remove metal ions include marine algae, fungi, bacteria, agricultural residues, and biopolymers [12–16]. Biosorption of Cr(VI) from aqueous solutions

such as industrial effluents, polluted wastewater etc. can be obtained using algal biomass [7, 17–19].

It has been reported that the organic substances from untreated algae are leached out during the biosorption process. Organic leaching results in secondary contamination and the leachate may lose some useful adsorption components that reduce the biosorption capacity. Therefore, it is recommended to treat the algae physically and/or chemically prior to application. One of the pretreatment methods is encapsulation by which leaching can be avoided efficiently [9]. In the encapsulation technique, various supporting materials are used as stabilizing agents such as alginate, chitosan, agar, polyvinyl alcohol, and polyacrylamide [9, 20–25].

Alginate (Alg), a stabilizing agent, is a polysaccharide biopolymer extracted from brown algae and consists of 1,4-linked β -D-mannuronic acid and α -L-guluronic acid [26]. Sodium alginate has some good features such as biodegradability, bio-compatibility, and renewability. Alginate has a high affinity for toxic heavy metal ions due to the abundance of numerous carboxyl and hydroxyl groups [27, 28]. Physicochemical modifications such as composite formation can significantly improve the alginate adsorption properties due to the increasing number of surface functional groups. It can also modify its poor mechanical strength, stability and reusability [26]. In numerous studies, sodium alginate composite materials using nanomaterials, carbonaceous materials, some natural and synthetic polymers have been synthesized to increase the adsorption capacities for heavy metal ions [29–35].

Ulva fasciata is a green alga mainly contains cellulose in the cell wall, and a high content of proteins bonded associated with many polysaccharides [9]. The presence of functional groups such as hydroxyl, carboxyl, amino and sulfate give algae the efficiency to remove Cr(VI) [7, 9, 12]. In our previous study, we reported that *U. fasciata* has the ability to completely remove Cr(VI) from aqueous solutions [7].

To the best of our knowledge, *U. fasciata* biomass encapsulated into calcium alginate beads has not been previously used to remove Cr(VI) from aqueous solutions. Consequently, this is the first comparative study of calcium alginate beads and calcium alginate/*U. fasciata* biocomposite for potential removal of Cr(VI) from aqueous solutions using various isotherm and kinetic models defined by different error functions. In this study, calcium alginate beads were prepared and composite beads for fixing the green alga *U. fasciata* to alginate as a support matrix. In terms of comparing calcium alginate (CA) and calcium alginate/*U. fasciata* (CA/UF) adsorption mechanism, several parameters such as the pH, initial concentration, contact time and dose are taken into consideration during batch studies to evaluate the optimal parameters of their

adsorption process. The adsorption mechanism was confirmed using FTIR, SEM, EDAX, BET and BJH techniques as well as several error function methods to determine the best adsorption isotherm and kinetic models. Finally, studies of regeneration and reuse of the developed beads were also examined.

2 Materials and methods

2.1 Materials

Potassium dichromate, sodium alginate, calcium chloride, hydrochloric acid, and sodium hydroxide were purchased from May and Baker Ltd (England), Alpha Chemika (India), Oxford Lab Chem (India), Advent Chembio Pvt. Ltd. (India) and Qualikems Fine Chem Pvt. Ltd. (India). All required solutions were prepared using deionized water. The green alga *U. fasciata* was collected from the Eastern Harbor of Alexandria along the Egyptian Mediterranean Sea coast during 2018.

2.2 Preparation of calcium alginate beads (CA)

1% Sodium alginate solution was prepared by adding 1 g of sodium alginate to 100 mL of deionized water and the resulting solution was heated at 65 °C with constant stirring. After cooling, the solution was dropped into 200 mL of 0.1 M calcium chloride solution. The water-insoluble calcium alginate beads formed were solidified in calcium chloride solution for 24 h at 4 °C and then filtered, rinsed several times with deionized water and dried at 70 °C for 24 h [36].

2.3 Preparation of alga (*U. fasciata*)

After the alga was collected, it was washed with fresh water followed by distilled water to remove any adherent plants and residues. The alga was dried under shade and then in an oven at 65 °C for 24 h. The dried alga was ground and sieved to obtain a particle size of < 200 µm.

2.4 Preparation of calcium alginate/*U. fasciata* composite beads (CA/UF)

A 1 g of the powdered alga *U. fasciata* with a particle size < 200 µm was mixed with 100 mL of (1%, w/v) sodium alginate solution. The mixture was stirred for 1 h to obtain a homogeneous solution which was added in dropwise into 200 mL of 0.1 M calcium chloride solution and the resulting green composite beads were collected and processed as prepared CA beads [36, 37].

2.5 Preparation of Cr(VI) solution

A 1000 mg/L stock solution was prepared by liquefying potassium dichromate ($K_2Cr_2O_7$) in 1.0 L deionized water. Then concentrations of 25 to 200 mg/L of the stock solution were prepared. The Cr(VI) concentration was determined according to standard method of Gilcreas et al. using UV–Vis spectrophotometer (unico UV-2000) with a wavelength of λ 540 nm [38]. All adsorption experiments were performed at room temperature (25 ± 2 °C). Initial pH was adjusted with 0.1 N HCl and 0.1 N NaOH solutions.

2.6 Characterization of adsorbents

The surface morphology and elemental composition of the adsorbents CA and CA/UF were studied by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDAX) using Quanta 250 scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) spectra of CA and CA/UF before and after adsorption of Cr(VI) were characterized with a VERTEX 70 FTIR-Bruker spectrometer over the range 4000–400 cm^{-1} . The surface area, pore volume and mean pore diameter of the adsorbents were determined using a BET analyzer (BEL-SORP mini, BEL Japan, INC). BET and BJH analyses were performed by adsorption isotherm measurements based on Brunauer, Emmett and Teller (BET) theory at 77 K and saturated vapor pressure of 102.22 kPa nitrogen.

2.7 Batch adsorption studies

Hexavalent chromium adsorption to the surface of CA and CA/UF beads was performed in well-sealed bottles (100 mL) with a capacity of 25 mL of Cr (VI) solution under conditions of different initial chromium concentrations (25–200 mg/L), weight of adsorbents (0.1–0.75 g), pH (1–9) contact time, (30–360 min) and stirring speed (120 rpm). The percentage of Cr(VI) ions removed (% Re) at 25 ± 2 °C and the adsorbed amount of Cr(VI) ions per unit mass of the beads at time t q_t (mg/g) and at equilibrium q_e (mg/g) was calculated using the following equations Eqs. (1–3).

$$\%Re = \left(\frac{C_o - C_t}{C_o} \right) \times 100 \quad (1)$$

$$q_t = \frac{(C_o - C_t) \times V}{m} \quad (2)$$

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (3)$$

where, C_0 , C_t and C_e are the initial, specific contact time t and equilibrium Cr(VI) concentration in mg/L, V is the volume of solution (L), and m is the weight of adsorbent (g).

2.8 Adsorption isotherm and kinetic studies

The adsorption properties and equilibrium data, known as adsorption isotherms describe how Cr(VI) interacts with the adsorbent. In order to optimize the adsorption system design, it is important to establish the most suitable correlation of the equilibrium curve. In this study, experimental data were compared by using eleven well-known and widely applied isotherm equations in order to find the best fit model for the obtained data. These adsorption equilibrium theories are Langmuir, Freundlich, Temkin, Generalized, Dubinin-Radushkevich, Flory-Huggins, Non-ideal competitive adsorption, Redlich-Peterson, Radke-Prausnitz, Khan, and Brunauer-Emmett-Teller models that can describe equilibrium studies [14, 16, 39].

The adsorption rate which varies with the surface and pore properties of the adsorbent material was evaluated using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models to remove 25 mL of Cr(VI) solution under conditions of different initial chromium concentrations (25–200 mg/L), weight of adsorbents (0.5 g for CA and 0.75 g for CA/UF), pH 1, at $25 \pm 2^\circ\text{C}$, contact time, (30–360 min) and stirring speed (120 rpm) [16, 40].

2.9 Regeneration and reuse study

For desorption, 0.75 g of the spent adsorbent (CA/UF) was added to 20 mL of 0.1 N HCl and the mixture was shaken at 120 rpm at $25 \pm 2^\circ\text{C}$ for 2 h. The regenerated adsorbent was washed with distilled water after each sorption/desorption cycle until neutral pH was obtained, then the composite adsorbent was filtered and dried at 70°C and cooled at room temperature ($25 \pm 2^\circ\text{C}$) for reuse [41, 42].

2.10 Statistical analyses

Several statistical terms are used as a measure of accuracy and are defined as error functions. These functions are used to select the best fit data for isothermal and kinetic models [43]. Error functions are used to evaluate the validity of mathematical equations for isotherm and kinetic models with experimental adsorption results. In the current study, the best fit isotherm and kinetic model were evaluated by calculations of error functions including coefficient of determination (R^2), chi-square test (χ^2), average relative error (ARE), sum of squares of the errors (ERRSQ), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), residual root mean square

error (RMSE) and sum of absolute errors (EABS) [43]. Various error functions were examined, and in each case the variables for the isotherm and kinetic models were determined by minimizing the relevant error function over the studied concentration range. This process was performed using the Solver add-ins with Microsoft Excel 2010.

3 Results and discussion

3.1 Adsorbent characterization

Characterization of CA and CA/UF beads is performed by FTIR, SEM, EDAX, BET and BJH instrumental techniques. The active functional groups present in both adsorbents before and after Cr(VI) adsorption are identified by FTIR (Figs. 1, 2). From these figures, the binding mechanism of the studied adsorbents is explored. As shown in Fig. 1, the removal of Cr(VI) increases the intensity of the peaks of the active binding sites due to the swelling of CA during the adsorption process and the replacement of the linked calcium ions by chromium on the surface and the porous spaces in the beads [44, 45]. Further, the broad 3260.66 cm^{-1} of O–H stretching peak in the alginate molecule shifts and becomes sharper at 3361.68 cm^{-1} after chromium adsorption on CA. This may be attributed to the replacement of Ca and adsorption of water molecules [46]. The assigned band 2924.26 cm^{-1} of C–H bonds in the alginate beads becomes sharper at 2924.63 cm^{-1} after Cr(VI) adsorption due to incorporation of chromium into the alginate matrix [44]. The sharp peak that appeared strongly at 1721.34 cm^{-1} belongs to the C=O carbonyl vibration within the alginate molecule [46]. The shift and sharpness of the bands from 1589.30 and 1415.71 cm^{-1} before the absorption process to 1633.18 and 1407.16 cm^{-1} after adsorption may be accompanied by the asymmetric stretching of COO^- groups in CA and the electrostatic interaction of Cr(VI) with protonated carboxyl groups [46, 47]. In addition, the intense shift of the 1079.25 cm^{-1} sharp peak to the smaller wavelength 1029.26 cm^{-1} can be attributed to the symmetric and asymmetric stretching vibration of C–O and C–O–C bonds, respectively after chromium binding during adsorption process [35, 48]. Figure 2 shows the drastic decrease in the bands' intensity in CA/UF before and after adsorption, i.e. the increase in transmittance % at higher wavelengths, which attributes to the large number of groups especially, the association of carboxyl and hydroxyl groups with Cr(VI). This indicates the incorporation of chromium within the polysaccharide polymer [46]. However, it has been reported that shifts or changes in FTIR peaks may be related to the interactions between chromium and functional groups on the surface of

Fig. 1 FTIR of CA beads: **a** before and **b** after Cr(VI) adsorption

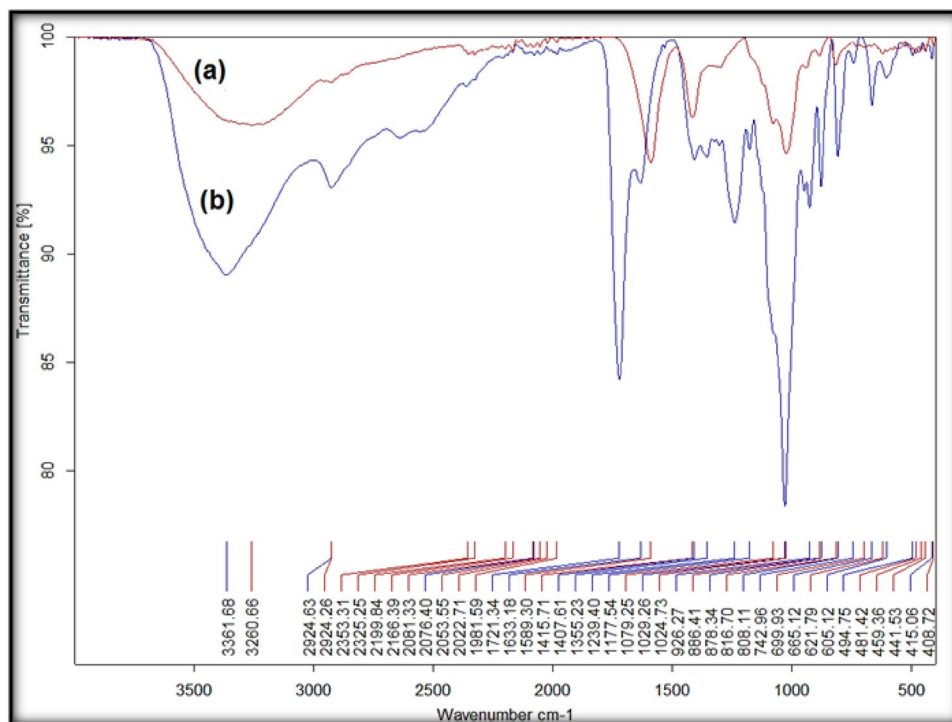
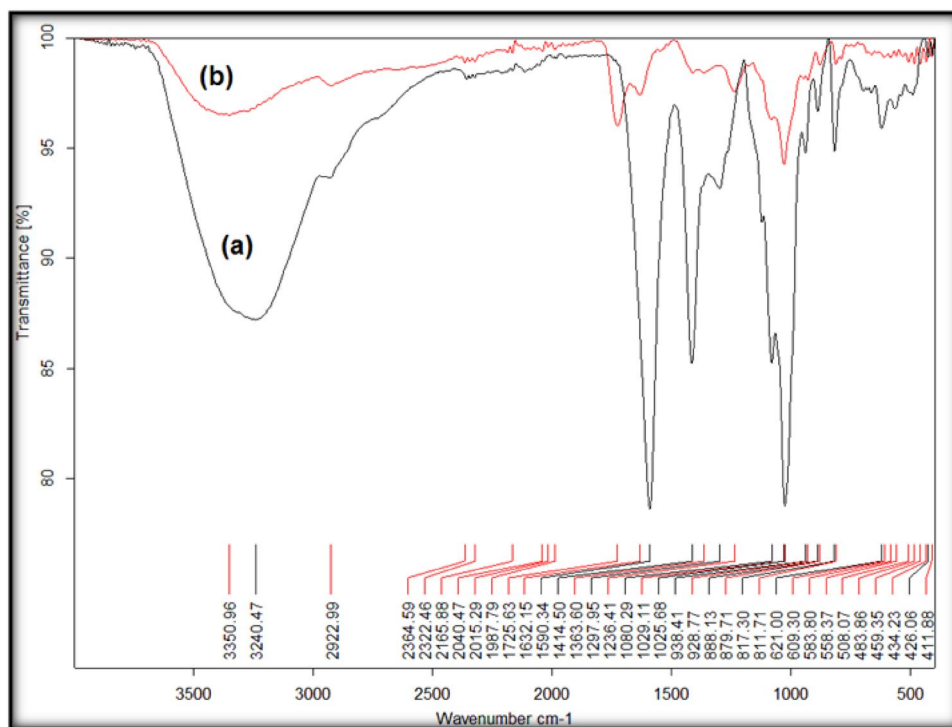


Fig. 2 FTIR of CA/UF beads: **a** before and **b** after Cr(VI) adsorption



adsorbent during the adsorption process or a chemical reaction [49]. These electrostatic interactions were previously demonstrated by the positive charge formed on alginate with the Cr(VI) as the dominant species of oxyanion (HCrO_4^-) at pH less than 2.5 [50].

The surface morphology and the elemental composition of CA and CA/UF are achieved by scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDAX). The EDAX spectra of CA and CA/UF after Cr(VI) adsorption are presented (Fig. 3a, b). The EDAX

spectra of CA and CA/UF show the increase in calcium ions from 0.07 to 0.19% confirming the increased calcium content due to the confinement of biomass retention of *U. fasciata* containing polysaccharides with calcium alginate in CA/UF beads (Fig. 3a, b). The enhancement of Cr(VI) uptake from 34.13 to 36.62%, while, the oxygen content retained around 30.91 and 29.62% in the CA and CA/UF beads, respectively, reflecting the contribution of the functional groups of polysaccharide polymer to chromium adsorption (Fig. 3a, b). Also the increase in Cr(VI) in CA/UF more than CA may be related to the replacement of Ca ions bounded to the carboxylic groups by Cr(III) on the surface and/or within the polysaccharide polymer in CA besides that in *U. fasciata* biomass during the Cr(VI) adsorption process (Fig. 3a, b; [50]). The slight change in the oxygen content may accompany with the swelling of CA/UF beads during the adsorption process. Scanning electron microscope (SEM) images of CA and CA/UF before and after Cr(VI) adsorption show the difference between their surface morphology (Fig. 4a–d). The surface of the CA beads at the beginning of the adsorption process is smooth with some cracks and porosity, while at the end of Cr(VI) sorption procedure the surface appears to be covered by the Cr(VI) ion species with some porosity (Fig. 4a, b). In case of CA/UF initially, the surface appears to be homogenous with algal particles with visible cracks. Whereas, after Cr(VI) removal experiment, the surface of the beads appears to be swollen with chromium solution and covered with Cr(VI) ion species with some distributed porosity (Fig. 4c, d).

The specific surface area, pore volume, mean pore diameter and mean particle size for CA and CA/UF are determined by isotherm measurements of N_2 adsorption–desorption under liquid nitrogen temperature using BELSORP mini, BEL Japan, INC, and at 77 K as an adsorption temperature. In this process, samples are pretreated at 140 °C under a nitrogen gas flow. The exact surface area, pore diameter, pore volume and mean particle size are calculated from the nitrogen adsorption isotherms based on Brunauer, Emmett and Teller (BET) theory. BET and BJH methods for CA using 0.5018 g with saturated vapor pressure and standard volume of 102.22 kPa and 0.354 cm³/g, respectively give a BET surface area, BJH surface area, total pore volume ($p/p_0 = 0.990$), and mean pore diameter of 1.542 m²/g, 1.481 m²/g, 0.001 cm³/g, and 4.94 nm, respectively. While for CA/UF, BET and BJH methods using 0.1680 g with saturated vapor pressure and standard volume of 102.19 kPa and 1.17 cm³/g, respectively give a BET surface area, BJH surface area, total pore volume ($p/p_0 = 0.990$), and mean pore diameter of 5.07 m²/g, 4.77 m²/g, 0.014 cm³/g, and 11.33 nm, respectively. It is noteworthy that the mean pore follows the meso-porous adsorbent pore width (2–50 nm) which

is adsorbed at a relative pressure close to unity (0.990) [51]. The presented BET and BJH data indicate the significant difference in particle size of CA and CA/UF beads. Thus, these data indicate that CA/UF beads possess a surface area three times larger than that of CA. Also, CA/UF beads have a mean pore diameter and total pore volume of about 2.3 and 14 times greater than those of CA. This confirms the importance of CA/UF in chromium removal. Our results are in consistence with the findings of Shetty et al. who demonstrated that the embedded chitosan in calcium alginate beads possesses improved surface area compared with that of chitosan alone which led to a better adsorption efficiency of the immobilized chitosan [29].

3.2 Effect of pH

The initial pH of a chromium solution is an important parameter that affects the biosorption of chromium ions [19, 52]. Adsorption of chromium ions on adsorbents (CA and CA/UF) was studied in the pH range from 1 to 9, while other extraction parameters were kept constant: adsorbent dosage: 0.3 g/25 mL; agitation time: 360 min; initial concentration of Cr(VI) ions: 50 mg/L and temperature 25 °C ± 2 °C. The adsorption of Cr(VI) ions was found to decrease with increasing pH and reached a maximum of % 51.5% removal for CA and 86.5% for CA/UF at pH 1 indicating the maximum biosorption capacity of CA/UF beads from CA (Fig. 5a, b). The high removal efficiency of CA/UF reflects the important role of entrapping UF into CA beads. Similar results have been reported for hexavalent chromium removal using other adsorbents with an optimum pH of 1.0 [17, 52].

Based on the pK_a values of guluronic and mannuronic acids, monomers of alginate, that have been reported to be 3.65 and 3.38, respectively [53], the alginate gel is positively charged at pH < 2.5, neutral at pH ≈ 3.0–3.5 and negatively charged at pH > 4.0. Therefore, at low pH values, the surface of the adsorbents containing carboxyl and hydroxyl groups are protonated and acquire positive charges and thus, allowing adsorption of Cr(VI) ions [54]. Chromium can exist in different forms such as $HCrO_4^-$, H_2CrO_4 , $Cr_2O_7^{2-}$, and CrO_4^{2-} depending on the pH [55–57]. El-Sikaily et al. [17] reported that adsorption of Cr^{6+} at pH < 3.0 was attributed to the electrostatic attraction between the negatively charged chromium species ($HCrO_4^-$) and the positively charged functional groups on the surface of adsorbent cell wall due to the presence of more positively charged functional groups [55]. However, at pH > 4 the adsorbent cell wall contains more negative charge functional groups that repel metal anions resulting in a lower percentage of Cr(VI) removal [55].

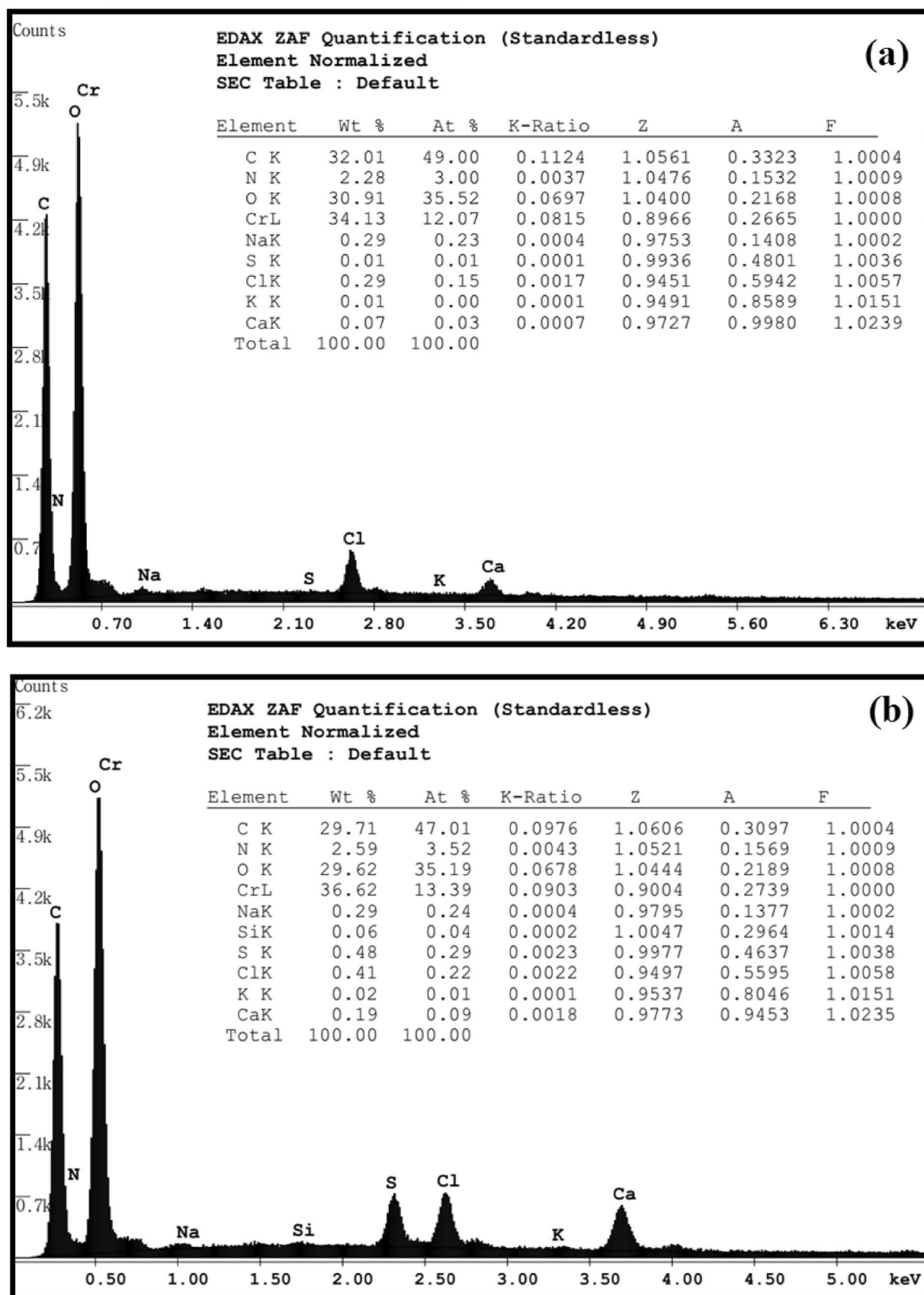


Fig. 3 EDAX of CA (a) and CA/UF (b) beads after Cr(VI) adsorption

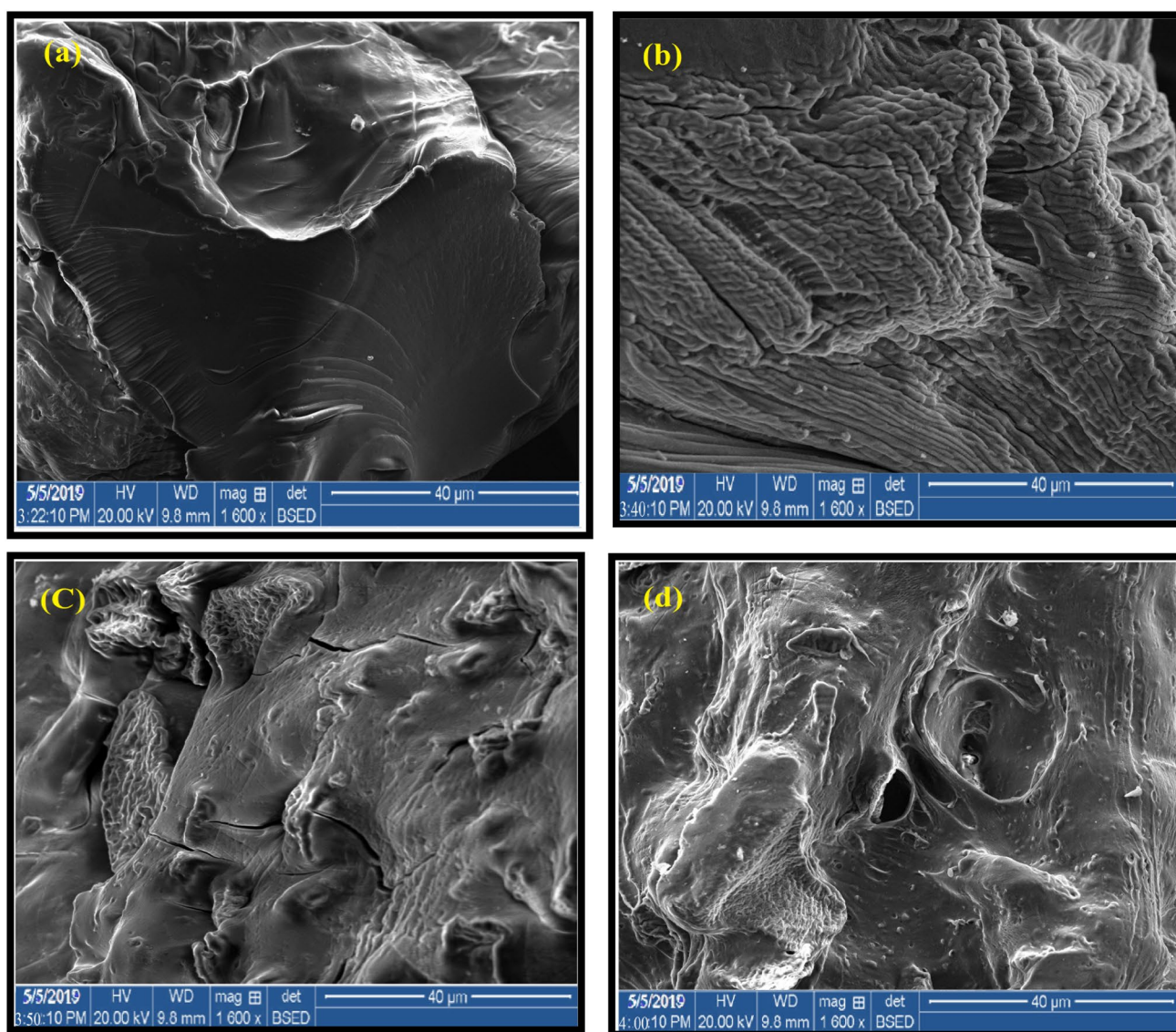


Fig. 4 SEM images of the CA beads: **a** before adsorption, **b** after adsorption and CA/UF beads, **c** before adsorption and **d** after adsorption of Cr(VI)

3.3 Effect of adsorbent dose

In the present study, the effect of adsorbent dose on the % removal of Cr(VI) ions was investigated by changing the adsorbent dose of CA and CA/UF from 0.1 to 0.75 g/25 mL at other constant conditions: pH 1; contact time: 360 min; initial concentration of chromium ions: 50 mg/L; and temperature: 25 ± 2 °C (Fig. 5c, d). The figure shows that for CA, the removal increases from 37.1% to 69.6% with increasing dose from 0.1 g/25 mL to 0.5 g/25 mL and then remaining constant at 0.75 g/25 mL. For CA/UF, when its amount increases from 0.1 g/25 mL to 0.75 g/25 mL, the removal significantly increases from 41.9% to 97.4%. This confirms the increased biosorption

activity of CA/UF compared to CA. However, the present results may coincide with the fact that when the dose of the adsorbents is increased the surface area and the number of active sites increase and after a certain dose a stationary phase is reached with a slight increase in the % removal [58]. This may be due to the accumulation or overlap of the adsorption sites with increasing dose of the adsorbent [59]. This can also be attributed to the difference in the porosity and surface area of the beads when loading a larger amount of the adsorbent [60]. As we mentioned previously, the present BET and BJH analyses reflect the larger surface area of CA/UF beads compared to CA. With the increase in the concentration of the metal adsorption solution, the beads become less

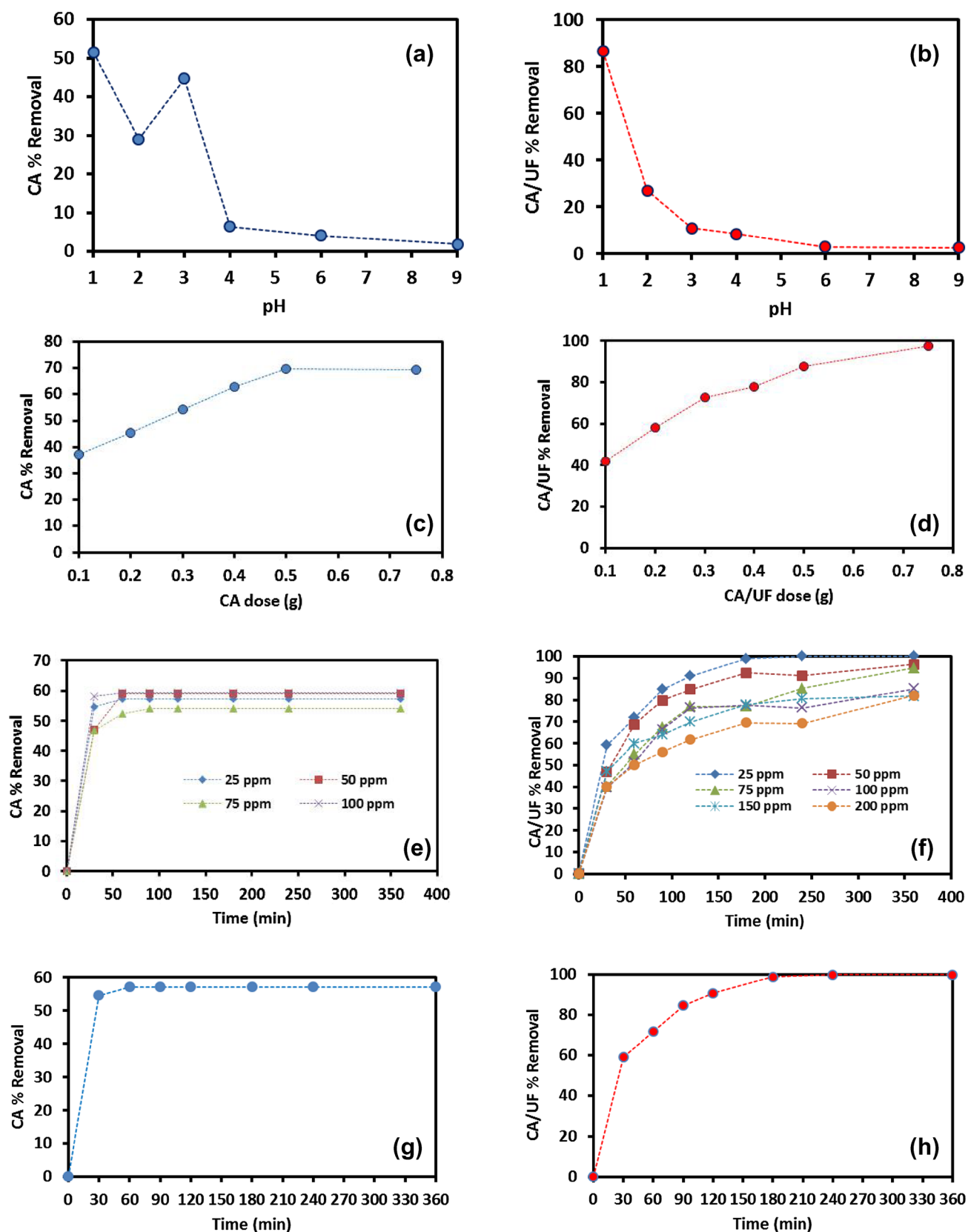


Fig. 5 Effect of pH (a, b), adsorbent dose (c, d), initial Cr(VI) concentration (e and f) and contact time (g and h) on the adsorptive removal of Cr (VI) by CA and CA/UF beads

porous and the free transport of metal ions to the internal adsorption sites is affected [60]. Thus, the porous amounts of beads are reduced along the total surface area due to their retention of metal ions [60].

3.4 Effect of initial Cr(VI) concentration

The effect of the initial concentration of Cr(VI) on the % removal of Cr(VI) ions was investigated by changing the initial concentration of Cr(VI) ions from 25 mg/L to 100 mg/L for CA beads and 25 mg/L to 200 mg/L for CA/UF beads, while keeping other parameters of the extraction constant (Fig. 5e, f). For CA, at time of 360 min and at initial concentrations of 25–100 mg/L, the removal of Cr(VI) slightly increases from 57.1 to 59.4% (Fig. 5e). This low observation of the efficiency of Cr(VI) removal by CA in the current study coincides with some previously mentioned studies [61, 62]. On the other hand, CA/UF beads show a gradual decrease in Cr(VI) removal for initial Cr(VI) concentrations 25–200 mg/L from 100 to 81.8% with a higher Cr(VI) removal percentage than CA beads (Fig. 5f). This may be due to the fact that at lower concentrations of Cr(VI) ions, the number of active sites for both adsorbents is more and therefore a higher removal of Cr(VI) ions is obtained [58]. But by increasing the concentration of Cr(VI) ions, the availability of active sites decreases which leads to lower removal. The higher Cr(VI) removal of CA/UF beads than that of CA beads may relate to their greater diameter, surface area, and higher amounts of trapped biomaterial [61, 62].

3.5 Effect of contact time

The effect of contact time on the % removal of Cr(VI) was studied by changing the contact time from 30 to 360 min, while keeping all other parameters constant: pH 1, sorbent dosage 0.5 g/25 mL for CA and 0.75 g/25 mL for CA/UF, initial Cr(VI) concentration 25 mg/L; and the temperature is 25 ± 2 °C (Fig. 5g, h). The results indicated that after 30 min contact time, 54.5% of removal is observed for the adsorbent CA beads and 59.1% for the CA/UF beads. Then, the % of removal is slowly increased and reaches a maximum of 75.0% after 360 min of contact with CA and 100% after 240 min of agitation with CA/UF. These results may be due to the fact that the active sites are initially available on the surface of the adsorbents, so the adsorption process is fast [62]. But as the active sites are gradually consumed over time, the % removal decreases and reaches a steady state after a certain period of time. The greater removal of Cr(VI) % by CA/UF beads than by CA attributed to the larger surface area and larger active sites of CA/UF beads, however, as discussed before the

encapsulation of *U. fasciata* biomass into CA leads to more beads diameter and adds more active sites [62].

3.6 Regeneration and reuse

Regeneration of the spent adsorbent allowing multiple uses is a desirable feature to reduce the cost of the adsorption removal process for practical applications. The CA/UF adsorption efficiency for Cr(VI) after the first regeneration decreases from 97.4 to 89.1%, and a slight decrease in the efficiency is observed in the following two cycles (87.7 and 82.3%, respectively). The decrease in the adsorption efficiency may be attributed to the mass loss of the adsorbents and surface passivation after initial adsorption [63]. The regeneration study revealed that Cr(VI) loaded adsorbents can be effectively recycled using HCl treatment.

3.7 Isotherm adsorption models

The adsorption process has been described by various two-parameter linear isotherm models namely: Langmuir, Freundlich, Temkin, Flory–Huggins, Dubinin–Radushkevich, Generalized, Non-ideal competitive adsorption (NICA), and Brunauer–Emmett–Teller (BET). Two-parameter non-linear isotherm models namely: Langmuir, Freundlich, Temkin, and Generalized as well as three-parameter non-linear isotherms namely: Redlich–Peterson, Radke–Prausnitz, and Khan were also used. The adsorbed amount of Cr(VI) is calculated from the given relationship Eq. (3) [14–16, 64].

The effect of Cr(VI) concentration on adsorption by CA and CA/UF beads was achieved using 25 mL of 25, 50, 75, 100, 150 and 200 mg/L Cr(VI) at pH 1, 0.5 g (CA) and 0.75 g (CA/UF) beads weight, 25 ± 2 °C, 120 rpm and stirring time 90 and 180 min, respectively. The applicability of the adsorption models is estimated by three invoking statistical methods: coefficient of determination (R^2 ; Eq. 4), chi-square test (χ^2 ; Eq. 5) and error functions Eqs. (6–11). The error functions used are the average relative error (ARE), sum of squares of the errors (ERRSQ), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), residual root mean square error (RMSE) and sum of absolute errors (EABS) [43]:

$$R^2 = \frac{\sum (q_{cal} - q_{aexp})^2}{\sum (q_{cal} - q_{aexp})^2 + (q_{cal} - q_{exp})^2} \quad (4)$$

$$\chi^2 = \sum \frac{(q_{exp} - q_{cal})^2}{q_{cal}} \quad (5)$$

$$ARE = \frac{100}{p} \sum_{i=1}^p \left| \frac{q_{cal} - q_{exp}}{q_{exp}} \right|_i \quad (6)$$

$$ERRSQ = \sum_{i=1}^p (q_{e,cal} - q_{e,exp})_i^2 \quad (7)$$

$$HYBRID = \frac{100}{p-n} \sum_{i=1}^p \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \quad (8)$$

$$MPSD = 100 \left(\sqrt{\frac{1}{p-n} \sum_{i=1}^p \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i} \right) \quad (9)$$

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^p (q_{e,exp} - q_{e,cal})^2} \quad (10)$$

$$EABS = \sum_{i=1}^p (q_{e,exp} - q_{e,cal})_i \quad (11)$$

where, q_{cal} , q_{exp} and q_{aexp} are the calculated, experimental and averaged values of capacitance of the adsorbents q (mg/g) and $(i-p)$ are the number of data points. The fit of the non-linear adsorption and kinetic models is obtained when ARE values become less than 5, while, the preference of the linear and non-linear models is tested by the high values of R^2 ($0 < R^2 < 1$) and the small amounts of χ^2 [65, 66]. Higher $ERRSQ$ and lower $EABS$ amounts provide a better fit for the adsorption graph.

3.7.1 Two-parameter linear and non-linear isotherm models

The equations belonging to the investigated adsorption isotherms are listed as follows Eqs. (12–23) [14–16]:

$$\text{Linear Langmuir} : \frac{1}{q_e} = \left(\frac{1}{K_L Q_m} \right) \frac{1}{C_e} + \frac{1}{Q_m} \quad (12)$$

$$\text{Non-linear Langmuir} : q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (13)$$

$$\text{Linear Freundlich} : \ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (14)$$

$$\text{Non-linear Freundlich} : q_e = K_f C_e^{1/n} \quad (15)$$

$$\text{Linear Temkin} : q_e = B_T \ln A_T + B_T \ln C_e \quad (16)$$

$$\text{Non-linear Temkin} : q_e = B_T \ln (A_T C_e) \quad (17)$$

Linear Flory–Huggins [67]:

$$\log \frac{\theta}{C_o} = \log K_{FH} + n_{FH} \log (1 - \theta) \quad (18)$$

$$\text{Linear Dubinin–Radushkevich} : \ln q_e = \ln q_{DR} - B \epsilon^2 \quad (19)$$

Linear Generalized [39]:

$$\ln \left(\frac{q_m}{q_e} \right) = \ln K_G - N_b \ln C_e \quad (20)$$

$$\text{Non-linear Generalized} : q_e = q_m \frac{C_e^{N_b}}{K_G + C_e^{N_b}} \quad (21)$$

Linear Brunauer–Emmett–Teller:

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{Q_{\max} C_{\text{BET}}} + \frac{C_{\text{BET}} - 1}{C_{\text{BET}} Q_{\max}} \cdot \frac{C_e}{C_s} \quad (22)$$

Non-ideal competitive adsorption (NICA) [65]:

$$\ln \left(\frac{q_e}{Q_{\max H} - q_e} \right) = n_H \ln C_e - \ln K_D \quad (23)$$

where, q_e and C_e represent the amount of Cr(VI) uptake per unit weight and the solution concentration at equilibrium.

Q_m and K_L are the monolayer adsorption affinity parameter and the Langmuir constant belonging to the adsorption energy Eqs. (12) and (13). Linear and non-linear Langmuir isotherm models for CA give relatively similar Q_m values of 416.67 and 401.67 (mg/g) with R^2 0.9858 and 0.9995, respectively; and a K_L of 0.01 L/mg (Tables 1 and 2). Linear Langmuir isotherm is applied to CA/UF beads giving $Q_m = 133.33$ (mg/g) and $K_L = 1.12$ L/mg with R^2 of 0.9260, while the non-linear form is not preferred (Tables 1 and 2). Although, more rapid removal of Cr(VI) by CA/UF is observed than CA beads, CA/UF beads show lower Q_m indicating multilayer adsorption along the heterogeneous surface. However, Langmuir isotherm postulates surface homogenous adsorption and the monolayer adsorption [68]. As it is generally known, the Langmuir isotherm is the most widely used isothermal equation due to its simplicity; it can only compare between different adsorbents but cannot explain the adsorption mechanism [68]. The preference of the Langmuir equation can be evaluated by the dimensionless separation factor (R_L) as follows Eq. (24) [64]:

Table 1 Values of isotherms for two-parameter linear adsorption models to remove Cr(VI) from 25–200 mg/L solutions on CA and CA/UF beads

Adsorption isotherm	Parameter	CA	CA/UF	Unit
Langmuir	Q_m	416.67	133.33	mg/g
	K_L	0.01	1.12	L/mg
	R^2	0.9858	0.9260	
	χ^2	0.22	1.72E+00	
Freundlich	K_F	1.15	39.46	(mg/g)/(mg/L) ⁿ
	n_F	0.84	2.43	
	R^2	0.9855	0.9680	
	χ^2	1.82	1.85E-02	
Temkin	A_T	0.15	6.23	l/min
	B_T	48.18	33.09	
	b_T	0.05	0.07	kJ/mol
	R^2	0.9985	0.8530	
Flory–Huggins	χ^2	5.92E-09	2.55E-10	
	K_{FH}	83.31	615.32	
	n_{FH}	0.75	0.70	
	ΔG	- 4.76	- 6.91	kJ/mol
Dubinin–Radushkevich	R^2	0.7076	0.9154	
	χ^2	0.25	1.88E-02	
	q_{DR}	109.13	117.41	mg/g
	B	0.00	1.00E-07	mol ² /kJ ²
Generalized	E	0.13	2.24	kJ/mol
	R^2	0.8798	0.7142	
	χ^2	6.28E-04	2.83E-04	
	N_b	0.94	0.74	
Brunauer–Emmett–Teller (BET)	K_G	128.43	1.18	mg/L
	R^2	0.9968	0.9277	
	χ^2	3.06E-05	1.94E-03	
	Q_{max}	14.75	135.14	
Non-ideal competitive adsorption (NICA)	C_{BET}	1.23	24.67	L/mg
	R^2	0.8775	0.8832	
	χ^2	3.10E-08	8.92E-06	
	K_d		2.01	mg/L
	K_a		0.31	
	n_H		0.60	
	R^2		0.9835	
	χ^2		4.38E-05	

$$R_L = \frac{1}{1 + K_L C_0} \quad (24)$$

Calculation of the R_L for initial Cr(VI) concentrations (C_0) 25, 50, 75, 100, 150 and 200 mg/L adsorbed on CA and CA/UF gives values less than one of 0.86, 0.75, 0.67, 0.60, 0.56 and 0.43, and 3.5E-02, 1.8E-02, 1.2E-02, 8.9E-03, 7.4E-03 and 4.4E-03, respectively, indicating the applicability of the Langmuir model in the CA and CA/UF adsorbents [69].

The linear form of Freundlich model gives a straight line describing the multilayer adsorption of Cr(VI) on the heterogeneous surface of CA with K_f and n_f values of 1.15 (mg/g)/(mg/L)ⁿ and 0.84, respectively (Eq. 14; Table 1)

however, the non-linear Freundlich model is not applied to CA (Eq. 15; Table 2). The n_f values are in the 1–10 range and reflect the availability of this adsorption model when the Cr(VI) concentrations are in the range of 25–200 mg/L [69, 70]. On the other hand, linear and non-linear forms of Freundlich isotherm are applied to adsorb 25, 50, 75, 100, 150 and 200 mg/L initial Cr(VI) concentrations on CA/UF giving different K_f values 39.46 and 29.15 and similar n_f values of 2.43 with R^2 0.9680 and 0.9997 and χ^2 of 1.85E-02 and 2.51E-04, respectively, reflecting greater applicability of the non-linear adsorption form (Tables 1 and 2). The results reflect that this non-linear form prefers an isotherm model to CA/UF with a higher R^2 (0.9997) value and a lower

Table 2 Values of isotherms and error functions for two-parameter non-linear adsorption models to remove Cr(VI) from 25–200 mg/L solutions on CA and CA/UF beads

Adsorption isotherm	Parameter	CA	CA/UF	Unit
Langmuir	Q_m	401.67		mg/g
	K_L	0.01		L/mg
	R^2	0.9995		
	χ^2	5.85E-03		
	ARE	2.71		
	ERRSQ	4895.8		
	HYBRID	1269.3		
	MPSD	356.3		
	EABS	8.81		
	RMSE	1.07		mg/g
Freundlich	K_F		29.15	mg/g
	n_F		2.43	L/mg
	R^2		0.9997	
	χ^2		2.51E-04	
	ARE		0.72	
	ERRSQ		12,196.5	
	HYBRID		3587.2	
	MPSD		598.9	
	EABS		3.15	mg/g
	RMSE		0.00	
Temkin	A_T		1.21	L/g
	B_T		33.29	
	b_T		0.07	kJ/mol
	R^2		0.9997	
	χ^2		3.08E-04	
	ARE		2.50	
	ERRSQ		13,788.5	
	HYBRID		4105.8	
	MPSD		640.8	
	EABS		6.33	
Generalized	K_G	130.17	3.17	mg/g
	Nb	0.84	0.90	
	R^2	0.9995	0.9996	
	χ^2	3.86E-03	2.07E-02	
	ARE	2.03	1.87	
	ERRSQ	4514.5	9409.6	
	HYBRID	1170.5	2537.4	
	MPSD	342.1	503.7	
	EABS	8.49	7.44	
	RMSE	0.03	0.12	mg/g

χ^2 (2.51E-04) value and indicate the multilayer adsorption of Cr(VI) ions on the heterogeneous CA/UF surface adsorbent [14–16].

The linear form of Temkin isotherm (Eq. 16; Table 1) that deals with the interactions between Cr(VI) and CA is

applied with a very low $\chi^2 = 5.92\text{E-}09$, while the non-linear form is not optimized (Eq. 17). Where, A_T value (0.15 l/min) refers to the low equilibrium binding constant, that is, the low binding energy required for the Cr(VI) adsorption [39] (Table 1). The value of B_T can be estimated from the relation: $B_T = (RT)/b_T$, where, T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol K), and the constant, b_T relates to adsorption heat [14]. The b_T of small value (0.05 kJ/mol) from the adsorption isotherm confirms the increase in the surface coverage of the CA adsorbent. In the case of CA/UF, linear and non-linear forms of Temkin isotherm also need small binding energy and demonstrate a high adsorbate approach [14] (Tables 1 and 2).

Linear Flory–Huggins isotherm can estimate the degree of surface coverage (θ) of the Cr(VI) on the CA and CA/UF (Table 1) [67]. The degree of surface coverage is $1 - C_e/C_0$, and the equilibrium constants K_{FH} and n_{FH} model are typical exponents from the intercept and slope of the linear straight line, respectively (Eq. 18). The K_{FH} value is used in calculating the free Gibbs non-spontaneous energy as given Eq. (25):

$$\Delta G^0 = -RT \ln (K_{FH}) \quad (25)$$

The negative ΔG^0 values obtained for CA and CA/UF -4.76 and -6.91 kJ/mol, respectively, reflect the spontaneity of Cr(VI) adsorption upon them (Table 1).

Linear Dubinin–Radushkevich isotherm can explain the physicochemical properties of the Cr(VI) adsorption on CA and CA/UF Eq. (19) [15]. The mean free energy of adsorption (E) and ε can be calculated from the following equations Eqs. (26 and 27):

$$E = \frac{1}{\sqrt{2B}} \quad (26)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (27)$$

where, R , T , and C_e are the gas constant (8.314 J/mol K), absolute temperature (K), and equilibrium concentration of Cr(VI) (mg/L), respectively. The plot of $\ln q_e$ versus ε^2 yields a straight line, in which, the values of q_{DR} and the mean free energy of adsorption E are calculated from the intersection and slope of the straight line, respectively. The value of E can predict the type of the adsorption, when, $E < 8$ kJ/mol and $8 < E < 16$ kJ/mol values refer to the types of physical and chemical ion-exchange, respectively [65, 71]. The calculated E values of 0.13 and 2.24 kJ/mol reflect the physical adsorption of Cr(VI) on CA and CA/UF, respectively (Table 1). The χ^2 and R^2 values (6.28E-04; 0.8798), and (2.83E-04; 0.7142) for CA and CA/UF, respectively can

explore the performance of adsorption process of Cr(VI) by this model on CA and CA/UF beads (Table 1).

Linear and non-linear forms of Generalized isotherm equations examine equilibrium data for Cr(VI) adsorption on CA and CA/UF (Eqs. 20 and 21; [14]). Where, K_G is the saturation constant (mg/L), N_b is the cooperative binding constant, and q_m is the maximum adsorption amplitude taken from Langmuir isotherm model (mg/g). The linear graphs of $\ln(q_m/q_e)$ versus $\ln C_e$ for CA and CA/UF give significant straight line ($R^2 \geq 0.9968$ and 0.9277 , respectively) and from the intercept and plot K_G (128.43 and 1.18 mg/L, respectively) and N_b amounts (0.94 and 0.74, respectively) (Table 1). In addition, the non-linear equation for CA gives relatively similar K_G values for the linear form (130.17 mg/L) and N_b (0.84) with a small ARE (2.03) value and different values for CA/UF (Table 2). Calculated quantities from linear and non-linear Generalized equations reveal to their applicability to remove Cr(VI) by CA and CA/UF (Tables 1 and 2).

The Brunauer–Emmett–Teller (BET) linear isotherm is estimated for the multilayer adsorption theoretical model Eq. (22) [15]. Where q_e is the amount of Cr(VI) adsorbed per unit weight of CA and CA/UF (mg/g) and C_e is the concentration of Cr(VI) remaining in the solution at equilibrium (mg/L). Whereas, C_s is the Cr(VI) saturation concentration (mg/L), Q_{max} is the amount of Cr(VI) adsorbed per unit weight of CA and CA/UF in complete monolayer formation on the surface (mg/g) and C_{BET} is the surface interaction energy constant (L/mg). The plots of $C_e/q_e (C_s - C_e)$ versus C_e/C_s for CA and CA/UF give straight lines of $R^2 \geq 0.8775$ and $\chi^2 = 3.10E-08$ and $R^2 \geq 0.8832$ and $\chi^2 = 8.92E-06$, respectively (Table 1). C_{BET} and Q_{max} are calculated from the intercept and slope, respectively (Table 1). These data for CA and CA/UF reflect the formation of the successive layers of Cr(VI) ions after the monolayer is completed.

The Non-ideal competitive adsorption (NICA) model reflects the cooperative phenomenon of the adsorption due to the ability of Cr(VI) ions to bind at one site on an adsorbent to influence Cr(VI) ions bound at another site on the same adsorbent (Eq. 23; [65]).

K_D , Hill constant which can be obtained from the given equation (Eq. 28):

$$K_D = K_d^{n_H} \quad (28)$$

where K_d , the dissociation constant per site (mg/L), is equal to the unadsorbed Cr(VI) content at half saturation ($K_d = C_e^{50}$). Also, $K_d = 1/K_a$, where, K_a is the association constant and n_H implies Hill cooperatively coefficient. Thus, three cases can be obtained; (i) $n_H > 1$, positive cooperative association, (ii) $n_H = 1$, non-cooperative or hyperbolic association (iii) $n_H < 1$, negative cooperative association [65].

The K_D and n_H values of the adsorption of Cr(VI) on CA/UF can be estimated from the intersection and slope of the graph, respectively and the K_d and K_a values are calculated (Table 1). The obtained $n_H < 1$ refers to the negative cooperative association of CA/UF [65]. However, the NICA model is not applied to CA beads. An executable NICA model for Cr(VI) removal by CA/UF with a value of χ^2 4.38E-05 and a value of R^2 0.9835 (Table 1).

Given the values of χ^2 , the applicability of two-parameter linear models for CA beads takes the descending order: Temkin > BET > Generalized > Dubinin-Radushkevich > Langmuir > Flory–Huggins > Freundlich (Table 1). The ARE and $RMSE$ values for the two-parameter non-linear form of Langmuir and Generalized models for CA beads indicate that the Generalized model is relatively more applicable than the Langmuir model (Table 2 and Fig. 6a). While, the two-parameter linear models for CA/UF give the descending order Temkin > BET > NICA > Dubinin-Radushkevich > Generalized > Freundlich > Flory–Huggins > Langmuir (Table 1). The two-parameter non-linear model for CA/UF beads takes the sequence Freundlich > Temkin > Generalized (Table 2 and Fig. 6b). The least preference of the two-parameter linear model of Langmuir model for Cr(VI) adsorption over CA/UF beads among other studied adsorption isotherm models, reflects the multi-layered adsorption mechanism of Cr(VI) ions [65].

3.7.2 Three-parameter non-linear isotherm models

The equations used for the three-parameter non-linear models that express the Cr(VI) adsorption procedure are given as Eqs. (29–31):

$$\text{Redlich–Peterson} : q_e = \frac{K_r C_e}{1 + a_r C_e^B} \quad (29)$$

Radke–Prausnitz [70]:

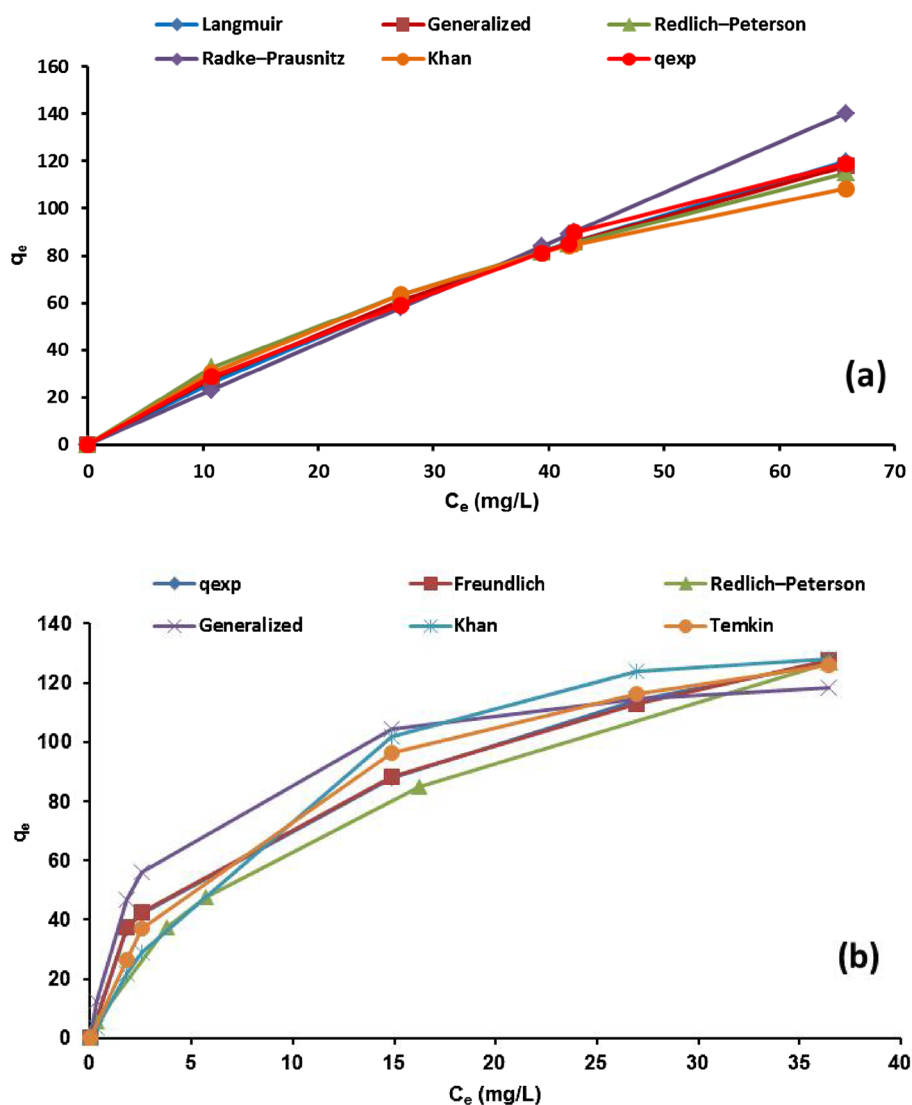
$$q_e = \frac{ARPC_e^d}{A + RC_e^{d-1}} \quad (30)$$

Khan [72]:

$$q_e = \frac{q_K b_K C_e}{(1 + b_K C_e)^{a_K}} \quad (31)$$

Redlich–Peterson isotherm expresses the heterogeneous multilayer adsorption systems at high adsorbate concentration, and also follows Henry's law at low concentration (Eq. 29; [65, 73]). This isothermal model is a proposed equation for the expression of Langmuir and Freundlich isotherms, thus represents both

Fig. 6 Graph of two-and three-parameter non-linear isotherm models for Cr(VI) adsorption on CA (a) and CA/UF (b)



heterogeneous and homogeneous adsorption systems [68]. The three Redlich–Peterson isotherm constants K_r , a_r , and B are calculated for Cr(VI) adsorption on CA and CA/UF (Table 3 and Fig. 6b). Calculations of the constants reflect the heterogeneous multilayer adsorption at high Cr(VI) concentration ($R^2 \geq 0.9994$, $\chi^2 = 5.20E-05$ and $ARE = 5.04$ for CA and $R^2 \geq 0.9997$, $\chi^2 = 7.23E-02$ and $ARE = 3.79$ for CA/UF with B values between 0 and 1 [65].

Radke–Prausnitz examines the heterogeneous equilibrium adsorption systems in dilute solutions Eq. (30) [70]. This model appears to be applicable to CA ($R^2 \geq 0.9997$, $\chi^2 = 1.63E-01$ and $ARE = 5.99$) with parameters of A , R_p , and d of 50.8, 0.04 and 0.33 values, respectively (Table 3).

The non-linear equation of Khan's adsorption balance is the general isotherm of pure solutions Eq. (31) [72].

Given the χ^2 values of CA for two- and three-parameter non-linear adsorption models, they take

the sequence Redlich–Peterson > Generalized > Langmuir > Khan > Radke–Prausnitz (Tables 2, 3 and Fig. 6a). For CA/UF the sequence follows Freundlich > Temkin > Khan > Generalized > Redlich–Peterson (Tables 2, 3 and Fig. 6b). The two-parameter non-linear form of Langmuir isotherm does not apply to CA/UF beads indicating multilayered adsorption of Cr(VI).

3.8 Adsorption kinetic models

Adsorption kinetics at a concentration of 25, 50, 75, 100, 150 and 200 mg/L Cr(VI) in 25 mL at pH 1, 0.5 g and 0.75 g adsorbent's dose for CA and CA/UF, respectively, and 30–360 min stirring time are carried out at $25 \pm 2^\circ\text{C}$. Three kinetic models namely; pseudo 1st order, pseudo 2nd order, and intra-particle diffusion are investigated Eqs. (32–36) [40, 74]:

Table 3 Values of isotherms and error functions for three-parameter non-linear adsorption models to remove Cr(VI) from 25–200 mg/L solutions on CA and CA/UF beads

Adsorption isotherm	Parameter	CA	CA/UF	Unit
Redlich-Peterson	K_r	7.24	27.20	L/g
	a_r	0.47	0.79	1/mg
	B	0.45	0.60	
	R^2	0.9994	0.9997	
	χ^2	5.20E-05	7.23E-02	
	ARE	5.04	3.79	
	$ERRSQ$	3761.8	12,393.1	
	$HYBRID$	975.3	3574.9	
	$MPSD$	312.3	597.9	
	$EABS$	17.20	20.10	
	$RMSE$	1.64	2.30	mg/g
Radke-Prausnitz	A	50.8		
	R_p	0.04		
	d	0.33		
	R^2	0.9997		
	χ^2	1.63E-01		
	ARE	5.99		
	$ERRSQ$	7656.5		
	$HYBRID$	1985.1		
	$MPSD$	445.5		
	$EABS$	34.86		
	$RMSE$	2.33		mg/g
Khan	q_K	215.80	513.70	mg/g
	b_k	0.02	0.03	
	a_k	1.00	2.00	
	R^2	0.9994	0.9997	
	χ^2	3.76E-02	6.10E-04	
	ARE	4.97	1.93	
	$ERRSQ$	3467.1	15,706.0	
	$HYBRID$	898.9	4635.3	
	$MPSD$	299.8	680.8	
	$EABS$	22.94	2.34	
	$RMSE$	0.77	0.15	mg/g

$$\text{Linear pseudo-first-order : } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (32)$$

$$\text{Non-linear pseudo-first-order : } q_t = q_e(1 - e^{-k_1 t}) \quad (33)$$

$$\text{Linear pseudo-second-order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (34)$$

$$\text{Non-linear pseudo-second-order: } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (35)$$

$$\text{Intra-particle diffusion : } q_t = k_p t^{1/2} + C_i \quad (36)$$

where, k_1 , k_2 and k_p are the rate constants of pseudo-first-order (1/min), pseudo-second-order (g/mg min), and intra-particle diffusion (mg/g min^{1/2}), respectively.

The adsorption mechanism of 25–200 mg/L Cr(VI) on 0.5 g CA beads appears to be more favorable with non-linear pseudo-first-order and linear pseudo-second-order models with χ^2 (2.00E-06–5.14E-02 and 2.00E-06–5.64E-02), $RMSE$ (0.22–4.54 and 0.22–4.57 mg/g) and ARE (8.53E-13–5.75E-02), respectively instead of linear pseudo-first-order and non-linear pseudo-second-order kinetic models (Table 4). Similar results confirmed that the calcium alginate encapsulated grape waste beads follow the pseudo-second order kinetic model [62]. This indicates that the adsorption process depends on the concentration of Cr(VI) on CA beads, however, k_1 and k_2 increase with Cr(VI) concentration. In addition, the amounts of $q_{e,exp}$ are relatively similar to those of $q_{e,cal}$ with values of k_1 and k_2 directly proportional to the concentration of Cr(VI). This validation finding is associated with large amounts of active sites on and inside the CA polymers.

Experimental adsorption data of 25–200 mg/L Cr(VI) on 0.75 g of CA/UF beads may reveal that linear pseudo-first-order, linear pseudo-second-order, and intra-particle diffusion kinetic models are the most applicable mechanisms ($\chi^2 = 1.01E-01$ – $2.83E+00$, $8.31E-31$ – $1.45E+00$ and $7.10E-07$ – $2.41E+00$, respectively) (Table 5), although the linear pseudo-second-order model cannot be applied when the values of q_{cal} are different from those of q_{exp} . For linear pseudo-first-order, the k_1 relatively increases with increasing Cr(VI) concentration from 25 to 200 mg/L. The performance of intra-particle diffusion model gives a straight linear line that doesn't pass through the origin with a deviation from the linearity. Also, the values of C_i increase with increasing Cr(VI) concentration, that is, with increasing thickness of the boundary layer due to swelling of the CA/UF beads [74]. This suggests that the intra-particle diffusion is a part of rate-limiting steps that are likely to continue at the same time [75]. Thus, the adsorption may undergo by ion exchange interaction and depends on the concentration of Cr(VI), and the ionic radius. Basically, the adsorption mechanism of Cr(VI) ions on CA/UF beads may involve a multi-stage process. As a result, the intra-particle diffusion model is applied to further explain the adsorption mechanism.

3.9 Comparative adsorption of CA and CA/UF beads

Adsorption rate constants with a concentration range of 25–200 Cr(VI) mg/L on CA beads are lower than those of CA/UF beads with the majority of adsorption (54.2–59.4%) observed with time ranges from 60 min

Table 4 Applied kinetic models for Cr(VI) adsorption on CA beads

Kinetic model			Rate constant		Kinetic equation	Statistical parameters							
Pseudo 1 st order			Cr(VI) (mg/L)	k ₁ (1/ min)	q _{cal} (mg/g)	R ²	χ ²	ERRSQ	HYBRID	MPSD	ARE	EABS	RMSE (mg/g)
Non-linear													
	25	0.184	28.56	q _t = 28.57(1-e ^{-0.184t})		0.9701	1.01E-03	0.2114	0.1490	3.8594	5.75E-02	1.1847	0.45
	50	0.384	59.01	q _t = 59.01(1-e ^{-0.384t})		0.8572	5.14E-02	20.6140	7.1959	26.8252	1.42E-04	12.0124	4.54
	75	0.515	81.25	q _t = 81.25(1-e ^{-0.515t})		0.7929	5.02E-02	27.8443	7.0265	26.5075	2.79E-06	13.9610	4.38
	100	0.715	118.83	q _t = 118.83(1-e ^{-0.715t})		0.8571	1.02E-03	0.8471	0.1430	3.7814	6.91E-09	2.4351	0.92
	150	0.915	215.58	q _t = 215.58(1-e ^{-0.915t})		0.8571	2.50E-04	0.3765	0.0350	1.8699	1.71E-11	1.6234	0.61
	200	1.015	268.59	q _t = 268.59(1-e ^{-1.015t})		0.9890	2.00E-06	0.0038	0.0003	0.1674	8.53E-13	0.8117	0.22
Pseudo 2 nd order													
	Cr(VI) (mg/L)	k ₂ (g/mg min)	q _{cal} (mg/g)	R ²	χ ²	ERRSQ	HYBRID	MPSD	ARE	EABS	RMSE (mg/g)		
Linear													
	25	0.064	28.57	t/qt = 1/(0.064 X (28.57) ²) + t/ 28.57		0.9999	1.21E-03						0.49
	50	0.001	59.09	t/qt = 1/(0.001 X (59.01) ²) + t/ 50.01		0.9834	5.64E-02						4.57
	75	0.005	81.25	t/qt = 1/(0.005 X (81.25) ²) + t/ 81.25		0.9998	5.02E-02						4.38
	100	0.035	118.83	t/qt = 1/(0.035 X (118.83) ²) + t/ 118.83		0.9999	1.01E-03						0.92
	150	0.054	215.58	t/qt = 1/(0.054 X (215.58) ²) + t/ 215.58		0.9999	2.50E-04						0.61
	200	0.173	268.59	t/qt = 1/(0.173 X (268.59) ²) + t/ 268.59		0.9999	2.00E-06						0.22
Non-linear													
	25	3.888	28.57	qt = (28.57 ² X 3.888t)/(1 + (28.57 X 3.888t))		0.7445	1.17E-03	0.2332	0.1643	4.0538	6.51E-01	1.3026	0.49
	50	4.527	59.01	qt = (59.01 ² X 4.527t)/(1 + (59.01 X 4.527t))		0.8582	5.12E-02	20.5539	7.1749	26.7861	2.91E+00	12.0164	4.54
	75	10.087	81.25	qt = (81.25 ² X 10.087t)/(1 + (81.83 X 10.087t))		0.7934	5.01E-02	27.8120	7.0183	26.4921	2.45E+00	13.9592	4.38
	100	14.087	118.83	qt = (118.83 ² X 14.087t)/(1 + (118.83 X 14.087t))		0.8596	1.01E-03	0.8374	0.1413	3.7596	2.94E-01	2.4420	0.92
	150	20.087	215.58	qt = (215.58 ² X 20.087t)/(1 + (215.58 X 20.087t))		0.8589	2.48E-04	0.3746	0.0348	1.8652	1.08E-01	1.6241	0.61
	200	26.087	268.59	qt = (268.59 ² X 26.087t)/(1 + (268.59 X 26.087t))		0.9884	1.93E-06	0.0036	0.0003	0.1642	4.33E-02	0.8136	0.22

Table 5 Applied kinetic models for Cr(VI) adsorption on CA/UF

Kinetic model		Rate constant		Kinetic equation	Statistical parameters		
Pseudo 1 st order	Cr(VI) (mg/L)	k_1 (1/ min)	q_{cal} (mg/g)		R^2	χ^2	RMSE (mg/g)
Linear							
	25	0.03	19.79	$\ln(19.79 - q_t) = \ln q_e - 0.03t$	0.8707	2.83E+00	10.28
	50	0.02	55.65	$\ln(55.65 - q_t) = \ln q_e - 0.02t$	0.9989	1.01E-01	4.51
	75	0.01	62.55	$\ln(62.55 - q_t) = \ln q_e - 0.01t$	0.8543	2.56E+00	18.63
	100	0.01	76.78	$\ln(76.78 - q_t) = \ln q_e - 0.01t$	0.9032	1.96E+00	22.20
	150	0.02	142.74	$\ln(142.74 - q_t) = \ln q_e - 0.02t$	0.9809	3.94E-01	15.98
	200	0.51	214.70	$\ln(199.51 - q_t) = \ln q_e - 0.51t$	0.9364	3.94E-01	20.02
Pseudo 2 nd order	Cr(VI) (mg/L)	k_2 (g/mg min)	q_{cal} (mg/g)		R^2	χ^2	RMSE (mg/g)
Linear							
	25	1.33E-03	33.33	$t/q_t = 1/(0.001 \times (33.33)^2) + t/33.33$	0.9982	3.33E-07	2.24
	50	6.03E-04	60.77	$t/q_t = 1/(0.001 \times (60.77)^2) + t/60.77$	0.9984	8.31E-31	3.56
	75	4.50E-04	96.65	$t/q_t = 1/(0.001 \times (85.50)^2) + t/85.50$	0.9032	1.45E+00	10.68
	100	2.91E-04	103.35	$t/q_t = 1/(0.0003 \times (101.82)^2) + t/101.82$	0.9940	2.32E-02	3.93
	150	1.86E-04	139.07	$t/q_t = 1/(0.0002 \times (135.43)^2) + t/135.43$	0.9884	9.76E-02	15.06
	200	1.74E-04	214.77	$t/q_t = 1/(0.0002 \times (199.51)^2) + t/199.51$	0.9989	1.17E+00	20.02
Intra-particle diffusion	Cr(VI) (mg/L)	k_p (mg/g min ^{1/2})	C_i		R^2	χ^2	RMSE (mg/g)
	25	1.41	13.41	$q_t = 1.41 \times t^{1/2} + 13.41$	0.9268	5.48E-03	2.83
	50	3.76	14.29	$q_t = 3.76 \times t^{1/2} + 14.29$	0.9268	7.10E-07	2.42
	75	4.10	24.24	$q_t = 4.10 \times t^{1/2} + 24.24$	0.9278	6.04E-01	16.33
	100	6.65	34.60	$q_t = 6.65 \times t^{1/2} + 34.60$	0.9412	2.41E+00	12.90
	150	5.90	54.14	$q_t = 5.90 \times t^{1/2} + 54.14$	0.9669	1.60E-03	4.70
	200	6.84	103.70	$q_t = 6.84 \times t^{1/2} + 103.70$	0.8941	6.04E-01	16.33

at low Cr(VI) (25–75 mg/L) concentrations to 30 min at higher concentration (100 mg/L). In case of CA/UF beads, the majority of adsorption observed (81.8–100.0%) over a time period of 120 min at low Cr(VI) concentrations (25–75 mg/L) and 180 min at higher concentrations (100–200 mg/L). This observation is coincident with the applied kinetic models of Cr(VI) adsorption on CA and CA/UF that is related to the change of beads properties from the non-encapsulated type to encapsulated type showing increased surface area, total pore volume, and mean pore diameter from (1.54 m²/g, 0.001 cm³/g and 4.94 nm) to (5.07 m²/g, 0.014 cm³/g and 11.33 nm) for CA, and CA/UF beads, respectively. Increased Cr(VI) adsorption phenomenon was previously achieved from bare to coated CA [62]. In addition to the different characterization between the type of beads, the enhancement of Cr(VI) adsorption may be associated with the partial reduction of Cr(VI) to Cr(III) by electron donors exist on the surface of the encapsulated algae. The reduced form of Cr(VI) interacts with the carboxylic groups of guluronate and mannuronate in the alginic

structure and in the algal substance, along with other functional groups present such as hydroxyl and amino [62]. Although Cr(III) is involved in the process of chromium adsorption from its Cr(VI) solution by substitution of released Ca²⁺, HCrO₄⁻ appears to be the most predominant Cr(VI) adsorbed species on the CA and CA/UF beads in the strong acidic medium (pH 1), however, this suggestion is also previously proposed [50]. In the current study, EDAX and FTIR analyses confirm the presence of the high oxygen and carbon contents more than calcium ions responsible for the interaction of Cr(III) with carboxyl groups [50]. Figure 7 represents the systemic diagram proposed for the current adsorption of Cr(VI) by CA and CA/UF taken from the expected similar mechanism for adsorption of Cr(III) and Cr(VI) ions on grape stalk powder trapped in CA [50]. Also, similar results previously revealed that the adsorption of Cr(VI) was related to both Cr(VI) adsorption and Cr(VI) partial reduction as well as the amount of functional groups present in the biomass [49].

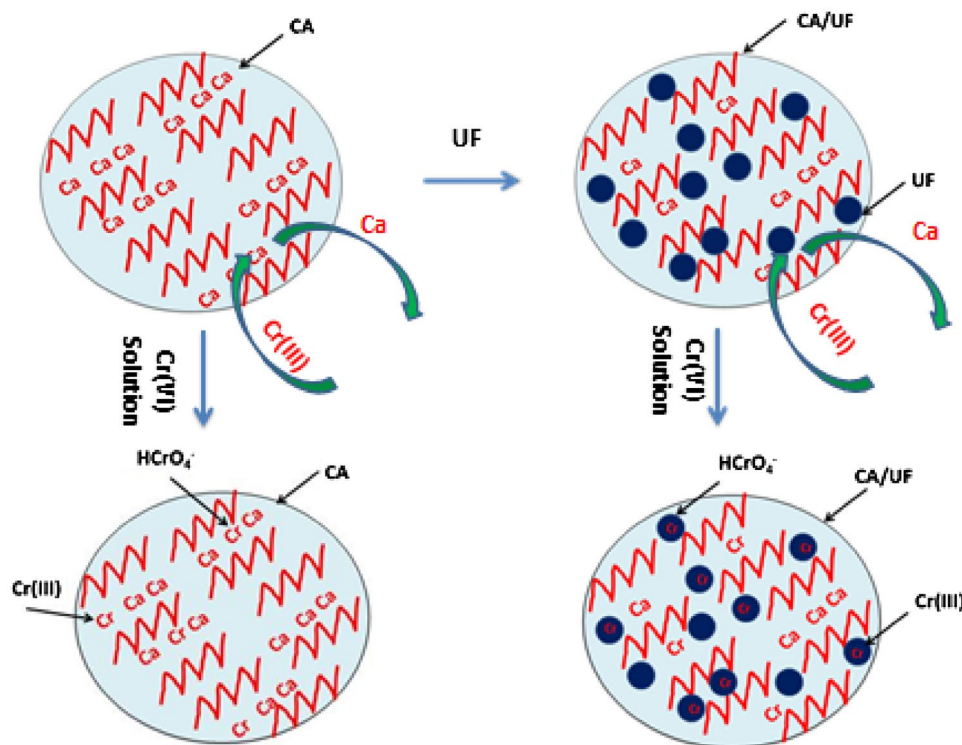


Fig. 7 The proposed schematic diagram of Cr(VI) adsorption on CA and CA/UF beads. The round circles represent the CA and CA/UF beads; the zigzag shapes represent the calcium alginate structure in CA and CA/UF; the round blue circles represent the *U. fasciata* algae immobilized in CA/UF beads. This schematic diagram includes several steps either consecutive and/or simultaneously: (1) partial reduction of Cr(VI) to Cr(III), meanwhile, HCrO_4^- appears

to be the most dominant chromium species, which replaces Ca^{2+} in CA and CA/UF beads, (2) diffusion of the Cr(VI) solution through the CA and CA/UF beads, and (3) incubation of the formed Cr(III) inside CA and CA/UF beads. The adsorption process on CA and CA/UF beads is based on different interactions such as: ion exchange, electrostatic attractions, physical adsorption, etc.

Table 6 Comparison of the maximum adsorption capacity of CA and CA/UF with other reported adsorbents

Adsorbent	Q_m (mg/g)	References
Magnetized graphene oxide ($\text{GO-Fe}_3\text{O}_4$)	3.197	[76]
Zirconium oxide-immobilized alginate beads (HZO@AB)	9.80	[42]
AOrGO-Ca composite	46.90	[30]
Alga <i>U. fasciata</i>	47.62	[7]
PANI/PVA/SA composite	83.10	[31]
PRrGO-Ca composite	89.90	[30]
Cellulose (DEMBC)	99.03	[77]
Cellulose (WEMBC)	102.89	[77]
Mn/SA-C	104.50	[32]
Sodium alginate fiber biochar loaded with lanthanum	104.90	[33]
CTS/CuS-25	116.76	[35]
Calcium alginate/ <i>Ulva fasciata</i> composite (CA/UF)	133.33	This study
Calcium alginate beads (CA)	416.67	This study

3.10 Comparison of adsorption capacity of CA and CA/UF with various reported adsorbents

The maximum sorption capacities of various adsorbents for Cr(VI) reported in previous studies are compiled in Table 6.

The adsorption capacities displayed by CA and CA/UF composite are better than that obtained by other reported adsorbents. The characterization results of CA/UF indicate that the composite has several binding groups and large surface area which are appropriate for Cr(VI) adsorption and

markedly enhance the process of removal. Additionally as previously mentioned in the subSect. 3.7.1., the postulated Langmuir isotherm for the monolayer homogenous adsorption mechanism is the least suitable isotherm model for CA/UF beads among the studied isotherms, although it is the most notable for its simplicity with different adsorbents. Thus, the smaller Q_m value of CA/UF in the current study than that of CA matches the results of the studied kinetic models and instrumental results that reflect the complexity of the adsorption mechanism which involves a multi-step and a multi-layer adsorbate formation (Table 6).

4 Conclusion

A comparative study was conducted on the removal of Cr(VI) by calcium alginate (CA) and *U. fasciata* biomass encapsulated in calcium alginate beads (CA/UF). This comparison was the first study to examine the appropriate adsorption mechanism of Cr(VI) adsorption on CA and CA/UF beads. The studied instrumental analyses including FTIR, SEM, EDAX, BJH and BET confirmed the greater Cr(VI) removal performance by CA/UF compared to CA.

The removal efficiency (%) was found to be 86.5% and 51.5% for CA/UF and CA, respectively at pH 1. The quantitative results of variable dose showed an increase in the Cr(VI) removal for CA from 37.1% to 69.6% as the dose increased from 0.1 to 0.5 g, while, for CA/UF, the removal enhanced significantly from 41.9% to 97.4% as the dose increased from 0.1–0.75 g. On the other hand, CA/UF beads showed a gradual decrease in the removal % from 100 to 81.8% for the initial Cr(VI) concentrations 25–200 mg/L but still higher than that of CA beads. Moreover, after 30 and 240 min of agitation, the removal by CA/UF was higher (59.1% and 100%, respectively) than that by CA after (30 min: 54.5% and 360 min: 75.0%), respectively. The regeneration experiments showed that the adsorption efficiency of CA/UF composite decreased to 82.3% after three cycles.

The adsorption process was evaluated by using various two-parameter linear isotherm models namely: Langmuir, Freundlich, Temkin, Flory–Huggins, Dubinin–Radushkevich, Generalized, Non-ideal competitive adsorption (NICA), and Brunauer–Emmett–Teller (BET). Two-parameter non-linear isotherm models namely: Langmuir, Freundlich, Temkin, and Generalized in addition to three-parameter non-linear isotherms namely: Redlich–Peterson, Radke–Prausnitz, and Khan were also used.

Adsorption by CA beads followed the pseudo- first-order and pseudo-second-order mechanisms, while, the intra-particle diffusion was specifically related to CA/UF beads besides the pseudo- first-order model. The observation of the applied kinetic models of Cr(VI)

adsorption on CA and CA/UF beads was simultaneous with a change in the properties of the beads from the non-encapsulated type to encapsulated type. This was due to the increased surface area, total pore volume, and mean pore diameter from (1.54 m²/g, 0.001 cm³/g and 4.94 nm) to (5.07 m²/g, 0.014 cm³/g and 11.33 nm) for CA and CA/UF beads, respectively.

From the presented study, it can be concluded that *U. fasciata* biomass encapsulated in calcium alginate beads CA/UF can be efficiently utilized in the Cr(VI) removal more than CA. Thus, it is advantageous to use the most practical eco-friendly adsorbents known for the lowest cost and the highest efficiency for removing toxic metals.

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Author contribution AHS did the following: conceptualization, methodology, data processing, formal analysis, writing original draft, investigation and validation, supervision, writing review and editing. GFEI-S did the following: conceptualization, methodology, data processing, formal analysis, writing original draft, investigation and validation, supervision, writing review and editing. Both authors contributed to the article and approved the submitted version.

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Data availability The datasets used and/or analyzed during the current study are available in this published paper.

Declarations

Conflict of Interest The authors have no competing interests to declare that are relevant to the content of this article.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish It is a pleasure for all the authors to publish the paper in this valuable journal.

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